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# Microwave-assisted Organic Synthesis

One Hundred Reaction Procedures



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# Preface

Microwave irradiation is a rapid way of heating materials for domestic, industrial and medical purposes. Microwaves offer a number of advantages over conventional heating such as non-contact heating (reduction of overheating of material surfaces), energy transfer instead of heat transfer (penetrative radiation), material selective and volumetric heating, fast start-up and stopping, and last but not least a reverse thermal effect, in which heat starts to build up from the interior of the material body.

The emergence of microwave-enhanced chemistry as an alternative, more efficient and environmentally friendlier way of performing chemical synthesis promises to be one of the most significant events of the 1990's with tremendous potential for the 21st century. More recently, it has been realized that some features of microwave irradiation i.e., solvent-free reactions, low-waste, energy efficiency, high yield, short reaction time, and usage of alternative solvents, can play an important role in the development of Green Chemistry methods.

This book is written primarily to help students at undergraduate and graduate levels to understand and apply microwave techniques to organic synthesis, using commercially available microwave reactors. It is hoped that the application of different kind of microwave reactors will help to spread ideas of microwave technologies. It should also serve as an introduction to the field for the industrial chemists with no prior training in microwave assisted organic chemistry.

The book will provide an introduction to the theory of microwave chemistry as well as practical laboratory manual by describing the methods of making a large number of compounds. Listing of the chemicals and equipment used in the syntheses and descriptions of the procedures and even the postsynthetic analyses will be very useful for the readers help them to design their own microwave reactions.

In the book, each experiment is introduced with a short discussion of associated hazards, the required equipment and its use, full operating procedure, physical properties of the expected product and extensive references to the source of the preparation and to related published work. Each procedure is checked to help and encourage students to use microwave techniques in the future. A number of methods from the literature which seemed attractive at first sight, are not exemplified in this book, either because they could not be reproduced at all by us or because they appeared to be impractical when performed.

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Dariusz Bogdał

# Chapter 1

## Interaction of microwaves with different materials

Microwaves are electromagnetic radiation placed between infrared radiation and radio frequencies, with wavelengths of 1 mm to 1 m, which corresponds to the frequencies of 300 GHz to 300 MHz, respectively. The extensive application of microwaves in the field of telecommunications means that only specially assigned frequencies are allowed to be allocated for industrial, scientific or medical applications (e.g., most of wavelength of the range between 1 and 25 cm is used for mobile phones, radar and radio-line transmissions). Currently, in order not to cause interference with telecommunication devices, household and industrial microwave ovens (applicators) are operated at either 12.2 cm (2.45 GHz) or 32.7 cm (915 MHz). However, some other frequencies are also available for heating [1]. Most common domestic microwave ovens utilize the frequency of 2.45 GHz, and this may be a reason that all commercially available microwave reactors for chemical use operate at the same frequency.

Heating in microwave cavities is based upon the ability of some liquids and solids to absorb and transform electromagnetic energy into heat. In general, during the interaction of microwaves with materials three different behaviors of a material can be observed depending whether the material is counted among:

- electrical conductors (e.g, metals, graphite - Fig. 1.2a)
- insulators, which are considered as materials with good dielectric properties (extremely poor conductors)(e.g., quartz glass, porcelain, ceramics, Teflon - Fig. 1.2b)
- lossy dielectrics, which are materials that exhibit so called dielectric losses, which in turn results in heat generation in an oscillating electromagnetic field (e.g., water - Fig. 1.2c)

When a strongly conducting material (e.g., a metal) is exposed to microwave radiation, microwaves are largely reflected from its surface (Fig. 1.2a). However, the material is not effectively heated by microwaves, in response to the electric field of microwave radiation, electrons move freely on the surface of the material, and the flow of electrons can heat

the material through a resistive (ohmic) heating mechanism. In opposite, in the case of insulators (e.g., porcelain), microwaves can penetrate through the material without any absorption, losses or heat generation. They are transparent to microwaves (Fig. 1.2b).

For some dielectrics, the reorientation of either permanent or induced dipoles during

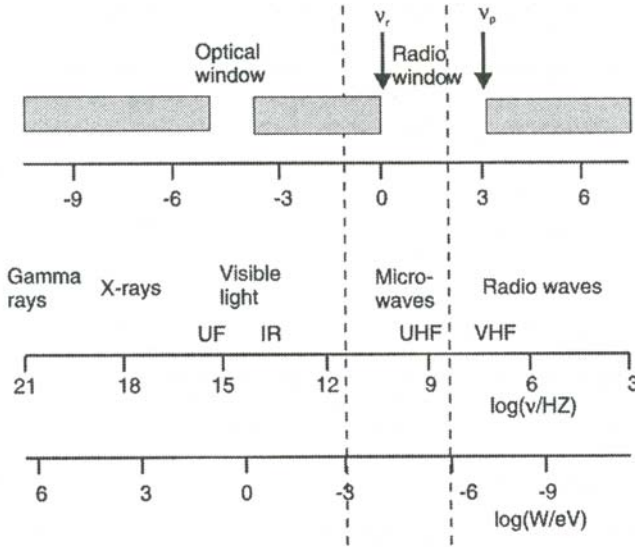


Figure 1.1. Spectrum of electromagnetic radiation:  $\lambda_0$  - wavelength in free space,  $W = h\nu$  quantum energy,  $\nu_r$  - lowest resonance frequency in the rotational spectrum of water,  $\nu_p$  - plasma frequency of the ionosphere. Reprinted with the permission from [2].

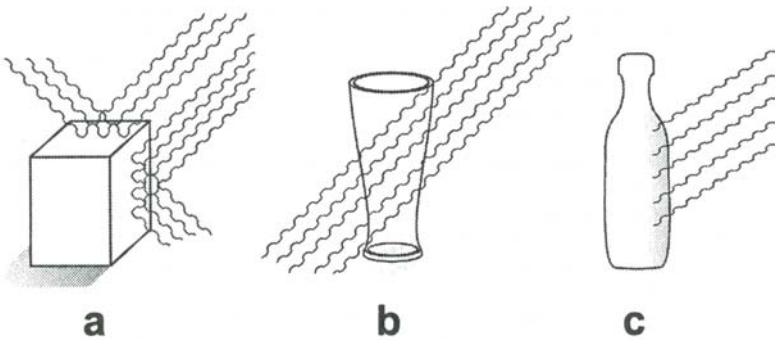


Figure 1.2. Interaction of microwaves with different materials: (a) - electrical conductor, (b) - insulator, (c) - lossy dielectric.

passage of microwave radiation which is electromagnetic in nature can give rise to absorption of microwave energy and heat generation due to the so called dielectric heating mechanism (Fig. 1.2c). Dependent on the frequency the dipole may move in time to the field, lag behind it or remain apparently unaffected. When the dipole lags behind the field (polarization losses) then interactions between the dipole and the field leads to an energy loss by heating (i.e., by dielectric heating mechanism), the extent of which is dependent on the phase difference of these fields.

In practice, most good dielectric materials are solid and examples include ceramics, mica, glass, plastics, and the oxides of various metals, but some liquids and gases can serve as good dielectric materials as well. For example, distilled water is a fairly good dielectric; however, possessing polar molecules (i.e., a dipole moment) can couple efficiently with microwaves to lead to heat generation due to polarization losses. Thus, such substances that are counted among dielectrics but exhibit some polarization losses that result in the dielectric heating are also called dielectric lossy materials or in general lossy materials. On the other hand, n-hexane, which having a symmetrical molecule, does not possess a dipole moment and does not absorb microwaves.

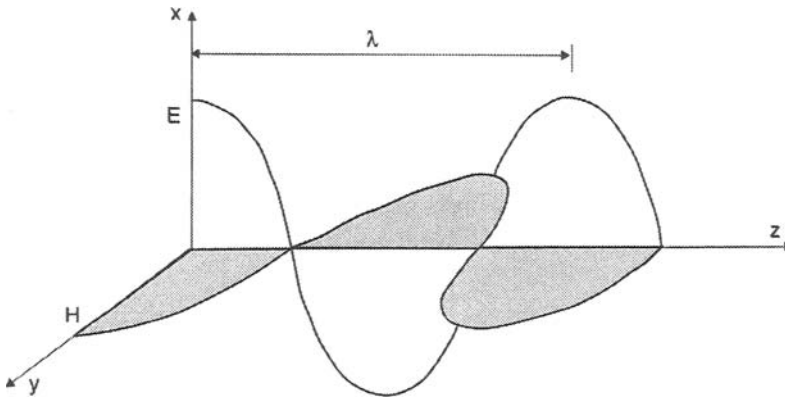


Figure 1.3. Electric (E) and magnetic (H) components during the propagation of electromagnetic waves. Reprinted with the permission from [1].

Microwave radiation, as all radiation of an electromagnetic nature, consists of two components, i.e. magnetic and electric field components (Fig. 1.3). The electric field component is responsible for dielectric heating mechanism since it can cause molecular motion either by migration of ionic species (conduction mechanism) or rotation of dipolar species (dipolar polarization mechanism). In a microwave field, the electric field component oscillates very quickly (at 2.45 GHz the field oscillates  $4.9 \times 10^9$  times per second), and the strong agitation, provided by cyclic reorientation of molecules, can result in an

intense internal heating with heating rates in excess of 10°C per second when microwave radiation of a kilowatt-capacity source is used [1]. Therefore, to apply microwaves to organic reactions, it is most important to find at least one reaction component that is polarizable and whose dipoles can reorient (couple) rapidly in response to changing electric field of microwave radiation. Fortunately, a number of organic compounds and solvents fulfill these requirements and are the best candidates for microwave applications.

To consider the application of microwave irradiation for organic synthesis, the first step is to analyze the reaction components together with their dielectric properties among which of the greatest importance is dielectric constant ( $\epsilon_r$ ) sometimes called electric permeability. Dielectric constant ( $\epsilon_r$ ) is defined as the ratio of the electric permeability of the material to the electric permeability of free space (i.e., vacuum) and its value can be derived from a simplified capacitor model (Fig. 1.4).

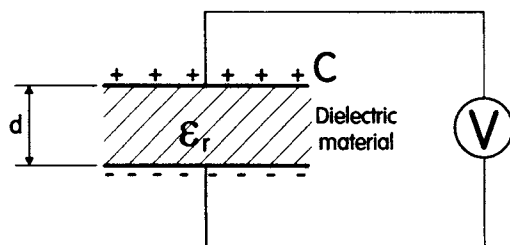


Figure 1.4. An electrical capacitor consisting of two metal plates separated by an insulating material called a dielectric.

When the material is introduced between two plates of a capacitor, the total charge ( $C_0$ ) stored in the capacitor will change ( $C$ ) (Eq. 1.1). The change depends on the ability of the material to resist the formation of an electric field within it and, finally, to get polarized under the electric field of the capacitor.

$$\epsilon_r = \frac{C}{C_0} \quad (1.1)$$

where:

- $C_0$  - the capacitance of the capacitor with vacuum
- $C$  - the capacitance of the capacitor with the material

Thus, dielectric constants ( $\epsilon_r$ ) that determine the charge holding ability of the materials are characteristic for each substance and its state, and vary with temperature, voltage, and, finally, frequency of the electric field. Dielectric constants for some common materials are given in Table 1.1.

Table 1.1

Dielectric constants ( $\epsilon_r$ ) of some common materials at 20°C .

Material	Dielectric constant( $\epsilon_r$ )	Material	Dielectric constant ( $\epsilon_r$ )
Vacuum	1	Titanium Dioxide	100
Air(1 atm)	1.00059	Water	80
Air(100 atm)	1.0548	Acetonitrile	38
Glass	5 - 10	Liquid ammonia(-78°C )	25
Quartz glass	5	Ethyl Alcohol	25
Porcelain	5 - 6	Benzene	2
Mica	3 - 6	Carbon Tetrachloride	2
Rubber	2 - 4	Hexane	2
Nylon	3 - 22	Plexiglass	3
Paper	1 - 3	Polyvinyl chloride	3
Paraffin	2 - 3	Polyethylene	2
Soil (dry)	2.5 - 3	Teflon	2
Wood (dry)	1 - 3	Polystyrene (foam)	1.05

Air has nearly the same dielectric constant as vacuum ( $\epsilon_r = 1.00059$  and 1, respectively). Polar organic solvents (i.e., water, acetonitrile, ethyl alcohol) are characterized by relatively high values of dielectric constants and, in turn, can be heated by dielectric heating mechanism under microwave irradiation. Non-polar organic solvents (i.e., benzene, carbon tetrachloride, n-hexane) have low dielectric constants and, in fact, show negligible heating effects under microwave irradiation. Most plastics range in the low values of dielectric constants (i.e., between 2 and 3), but some of these materials besides glass and quartz glass are used to manufacture reaction vessels for microwave application due to their good chemical as well as temperature resistance (e.g., Teflon, PET, PEEK).

However, in the case of highly oscillating electric fields and microwave applications, dielectric constant is turned into complex permeability ( $\epsilon^* = \epsilon' - j * \epsilon''$ ), which is a measure of the ability of dielectric materials to absorb and to store electrical potential energy. Like dielectric constant( $\epsilon_r$ ), which is commonly used to describe good isolators, the real permeability ( $\epsilon'$ ) component characterizes the ability of the material to be polarized by the electric field and thus the ability of microwaves to propagate into the material. At low frequencies this value reaches its maximum (i.e.,  $\epsilon_r$ ) since the maximum amount of energy can be stored in the material. The imaginary part of the complex electric permeability ( $\epsilon''$ ) is usually called the loss factor and indicates the ability of the material to dissipate the energy i.e. the efficiency of conversion of electromagnetic radiation into heat. The loss factor ( $\epsilon''$ ) reaches the maximum when the real permittivity ( $\epsilon'$ ) gradually decreases (Fig. 1.5). Obviously, it depends on the molecular structure of the material, on the frequency at which  $\epsilon''$  reaches its maximum and how distinctly this maximum is exhibited.



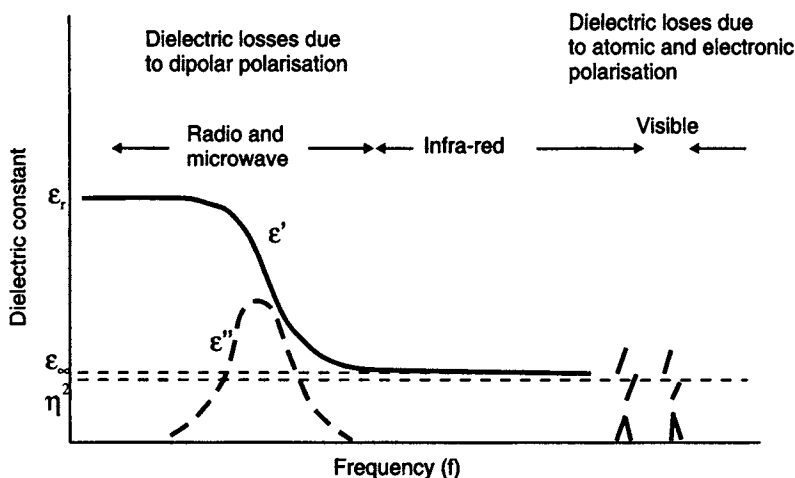


Figure 1.5. Relative real permittivity ( $\epsilon'$ ) and loss factor ( $\epsilon''$ ) depending on angular frequency of electromagnetic waves. Reprinted with the permission from [1].

The values of real permittivities ( $\epsilon'$ ) and loss factors ( $\epsilon''$ ) for some common organic solvents are given in Table 1.2.

Table 1.2

Real permittivities ( $\epsilon'$ ) and loss factors ( $\epsilon''$ ) of organic solvents at different frequencies at 20°C [3].

Solvent	$3 \times 10^8$ Hz		$3 \times 10^9$ Hz		$1 \times 10^{10}$ Hz	
	$\epsilon'$	$\epsilon''$	$\epsilon'$	$\epsilon''$	$\epsilon'$	$\epsilon''$
Water	77.5	1.2	76.7	12.0	55.0	29.7
0.1 M NaCl	76.0	59.0	75.5	18.1	54.0	30.0
Methanol	30.9	2.5	23.9	15.3	8.9	7.2
Ethanol	22.3	6.0	6.5	1.6	1.7	0.11
Propanol	16.0	6.7	3.7	2.5	2.3	0.20
Butanol	11.5	6.3	3.5	1.6	0.2	
Hexane	1.97		1.97	$2 \times 10^{-4}$	1.97	$9 \times 10^{-3}$
Carbon tetrachloride	2.2		2.2	$9 \times 10^{-4}$	2.2	$3 \times 10^{-3}$

Systematic solvent studies have disclosed the existence of a linear relationship between the polarity of the molecules (evaluated by their dielectric constants) and the temperature increase induced by microwave irradiation. The effect of microwave activation is therefore strongly dependent on the solvent nature, rather weak when non-polar solvents are employed, considerable with polar solvents, and large with strongly polar solvents, which

can be at the origin of very rapid heating [4].

Another commonly used term to characterize materials under microwave conditions is the loss tangent, ( $\tan \delta$ ), which is calculated as the ratio of  $\epsilon''$  and  $\epsilon'$  (Eq. 1.2, and this parameter even better describes the ability of a material to absorb microwave energy. At the same time, this ratio ( $\epsilon''/\epsilon'$ ) sometimes called the loss angle describes the phase difference between the electric field and the polarization of the material. The loss tangent and loss angle are always dependent on working frequency and temperature. The values of  $\tan \delta$  of some common organic solvents together with boiling points of the solvents and their temperatures after 1 min. of microwave irradiation are presented in Table 1.3.

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (1.2)$$

It can be seen (Table 1.2 and 1.3) that for optimum coupling (i.e., effective heating), a balanced combination of moderate  $\epsilon'$ , to permit adequate penetration, and high loss  $\epsilon''$  as well as  $\tan \delta$  are required [5]. The higher the loss tangent, the better the transformation of microwave energy into heat. However, water absorbs microwave efficiently at the frequency of 2.45 GHz has a high ability to transform microwave energy into heat, but it is worth stressing that alcohols are much better microwaves absorbers with values of the loss tangent ( $\tan \delta$ ) a couple of fold higher than the loss tangent ( $\tan \delta$ ) of water. Therefore, alcohols owing to lower values of heat capacity than water (c.f., water and ethyl alcohol heat capacities 4.18, 2.31 J/g °C, respectively [6]) can be heated with much higher heating rates than water to reach their boiling points in a shorter time (Table 1.3). Both water and alcohols can be added in a small amount to reaction mixtures in order to improve their dielectric properties (i.e., increase absorption of microwaves). DMF is also counted among good microwave absorbers. Therefore, instead of water or alcohols, it can be also added to reaction mixtures that are characterized by weak absorption of microwaves due to its higher boiling point. Non-polar solvents (e.g., hexane, carbon tetrachloride) are not a good subject for microwave activation; however, small amounts of them are added to reaction mixtures, in particular under solventless systems, in order to improve their temperature homogeneity during microwave irradiation.

The loss tangent ( $\tan \delta$ ) of some other common materials are presented in Table 1.4, while the loss tangent of water as the function of frequency is presented in Fig. 1.6 together with  $\epsilon'$  and  $\epsilon''$ . From Fig. 1.6 as well as Table 1.2, it is apparent that appreciable values of the loss factor ( $\epsilon''$ ) exist over a wide frequency range. For example, for water, the most effective heating as measured by  $\epsilon''$  reaches its maximum at ca. 20 GHz while most microwave ovens operate at a much lower frequency i.e., 2.45 GHz. The practical reason for the lower frequency is to heat the material throughout its interior. This is so that the radiation is not totally absorbed by the first layer of the material that it encounters and may penetrate further into the material, heating it more evenly. In the other words, if the frequency is optimal for maximum heating rate, the microwaves are absorbed in the outer region of the material and penetrate only a short distance (*skin effect*). Thus, for the reactions that are carried out under microwave conditions on larger

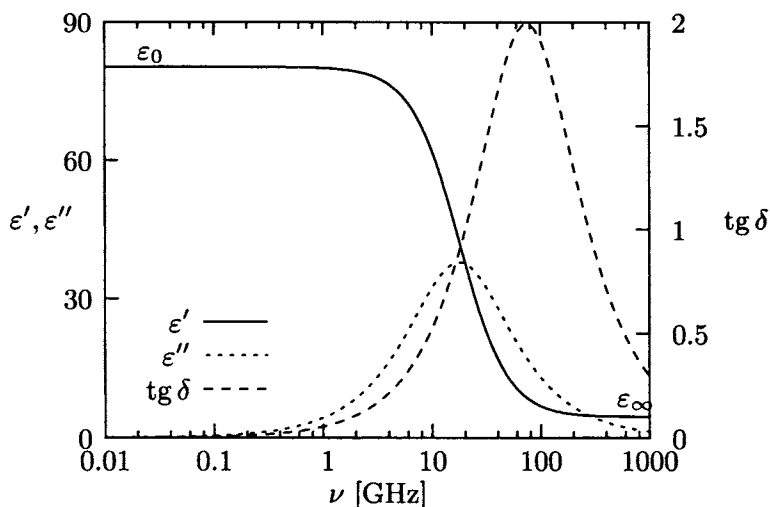


Figure 1.6. The loss tangent of water ( $\tan \delta$ ) as the function of frequency together with  $\epsilon'$  and  $\epsilon''$ . Reprinted with the permission from [7].

Table 1.3

Loss tangent ( $\tan \delta$ ) at 2.45 GHz (room temperature), boiling points and temperatures of common organic solvents after 1 min. of irradiation in a microwave cavity (50 ml of solvent, 1 min., power: 560 W) [7–9].

Solvent	Solvent temperature ( $^{\circ}\text{C}$ )	Boiling point ( $^{\circ}\text{C}$ )	Loss tangent $\tan \delta$
Water	81	100	0.12
Methanol	65	65	0.66
Ethanol	78	78	0.94
Propanol	98	97	0.76
Butanol	106	117	0.57
Ethyl acetate	73	77	0.06
Acetone	56	56	0.05
Acetic acid	110	118	0.17
DMF	131	153	0.16
Methylene chloride	41	41	0.04
Dioxane	53	101	-
Hexane	25	68	0.02
Carbon tetrachloride	28	77	-

Table 1.4

Loss tangents ( $\tan \delta$ ) of different materials at 25°C (2.45 GHz).

Material	Loss tangent $\tan \delta \times 10^{-4}$	Material	Loss tangent $\tan \delta \times 10^{-4}$
Quartz	0.6	Plexiglass	57
Ceramic	5.5	Polyester	28
Porcelain	11	Polyethylene	31
Phosphate glass	46	Polystyrene	3.3
Borosilicate glass	10	Teflon	1.5

scales, another important factor which describes the heating process is the penetration depth ( $D_p$ ) (Fig. 1.7) [1].

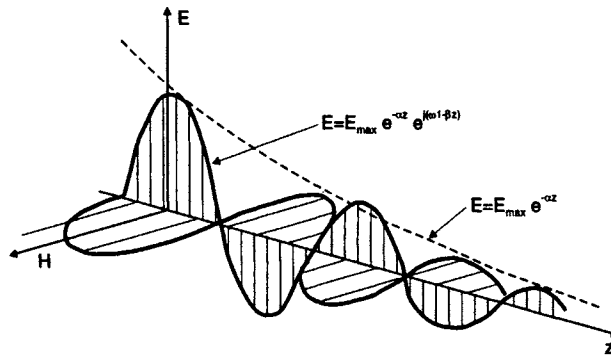


Figure 1.7. Propagation of electromagnetic waves in a lossy material. Reprinted with the permission from [1].

The penetration depth ( $D_p$ ) of the materials used to denote the depth at which the power density of microwave irradiation is reduced to 37% (i.e.,  $1/e$ ) of its initial value at the surface of the material. It is proportional to the wavelength of the radiation and depends on the dielectric properties of the material. For lossy dielectrics ( $\epsilon''/\epsilon' \ll 1$ ) the penetration depth ( $D_p$ ) can be calculated from Equation 1.3.

$$D_p = \frac{\lambda_o \sqrt{\epsilon'}}{2\pi \epsilon''} \quad (1.3)$$

- $\lambda_o$  - the length of electromagnetic wave
- $\epsilon'$  - the real permittivity
- $\epsilon''$  - the loss factor

Materials with relatively high values of the loss factor ( $\epsilon''$ ) are characterized by low values of the penetration depth ( $D_p$ ), and, therefore, microwaves can be totally absorbed within the outer layers of these material. For example, the penetration depth of water is 1.4 and 5.7 cm at 25 and 95°C, respectively (Table 1.5). This means that in the experiments in a water solution on larger scales only some parts (outer layers) of the reaction mixture interact with microwaves to generate heat which is then transported into the rest of the mixture conventionally (i.e., by heat convection and/or conduction mechanism). On the other hand, microwaves can penetrate and pass through the samples of the materials with low values of the loss factor ( $\epsilon''$ ). However, in the case of chemical reactions, this should not be treated as a drawback because due to the design of the microwave reactors unabsorbed radiation passing through the sample is mostly reflected back, and, finally, absorbed on later passes, which can provide enough energy to initiate a chemical reaction.

The heating rate (i.e., temperature increase) of the material under microwave irradiation depends also on the shape and size of the sample. For instance, the study of the thermal behavior of alumina indicate that the temperature of the sample during microwave irradiation depends on the amount of the sample (Fig. 1.8). In a multi-mode cavity, the maximum temperature was obtained for ca. 200 g of alumina since it had a larger surface and in turn could absorb more of the microwave energy per weight unit than, for example, 100 g of alumina. In contrast, the 500 g sample of alumina was heated with lower heating rate than 200 g sample, but in this case the most probable explanation is that 500 g of alumina consumed the entire microwave energy provided by the reactor, which in fact could be less per weight unit than for 200 g of alumina. Most likely, the amount of sample that would be heated most efficiently by microwaves under such experimental conditions was somewhere between 200 and 500 g of alumina. In turn, 4 g of alumina appeared as about the minimum amount for an appreciable thermal effect to be observed, while 1 g sample of alumina was unable to reach 100°C even after a relatively long irradiation time ca. 20 min [10].

Eventually, the sample size, penetration depth as well as heating rate are strongly coupled during microwave irradiation and may finally result in more homogeneous or heterogeneous heating of the material, which in turn can result in overheating of the material and creation of so called *hot spots* in the latter case.

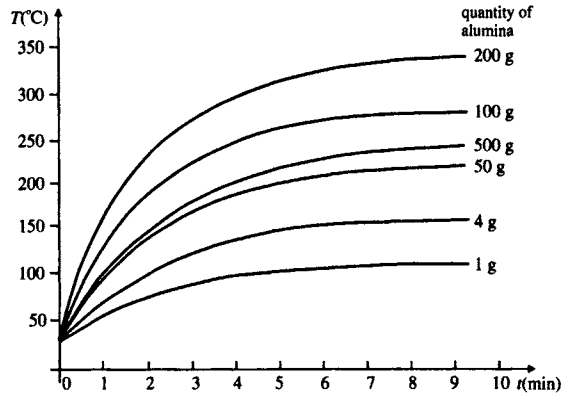


Figure 1.8. Thermal behaviour of neutral alumina as a function of irradiation time and quantity. Reprinted with the permission from [10].

Table 1.5  
Microwave (2.45 GHz) penetration depth ( $D_p$ ) in some common materials [11].

Material	Temperature (°C)	Penetration depth ( $D_p$ ) (cm)
Water	25	1.4
Water	95	5.7
Ice	-12	1100
Paper, cardboard	25	20..60
Wood	25	8..350
Rubber	25	15..350
Glass	25	35
Porcelain	25	56
Poly(vinyl chloride)	20	210
Epoxy resin (Araldite)	25	4100
Teflon	25	9200
Quartz glass	25	16000

## Chapter 2

# Microwave effect vs. thermal effect

Although the first publications concerned with the possibilities of use of microwave irradiation in organic synthesis appeared in 1980's [12,13] and in polymer chemistry even earlier at the end of 1960's [14], the sudden growth of interest in the application of microwave irradiation in almost all fields of chemistry took place at the end of 1980's. Nowadays, there is hardly find any reaction that has not been attempted under microwave conditions. The application of microwaves in chemistry is therefore so attractive that from the very beginning it was realized that a number of chemical processes can be carried out with a substantial reduction in the reaction time in comparison to conventional processes. Reactions that usually take many hours or days, under influence of microwave irradiation can be run in considerably shorter time of several minutes or even seconds [15]. These phenomena are not fully understood yet; however, there are two groups of theories that are proposed to explain the reduction of the reaction time under microwave conditions in comparison with processes under conventional conditions.

According to the first group of theories, in spite of the fact that the course of chemical processes under microwave conditions is considerably shorter than under conventional conditions, the kinetics and mechanism of the reactions are still the same. The reduction of the reaction time is the result of sudden and, sometimes, uncontrollable temperature growth of the reaction mixture under microwave irradiation, which in turn leads to the increase of reaction rates following common kinetic laws.

The second group of theories supposes that during microwave irradiation of the reaction mixture there is a specific effect of microwave activation that causes an increase of the reaction rates for which the bulk temperature of the reaction mixture is an inadequate to explain. Such an effect has been accepted to be called the *non - thermal microwave effect* or the *specific microwave effect*. Recent critical reviews concerned with both group of theories have been published by Loupy et al. [16], Nuchter et al. [17], and de la Hoz et al. [18], respectively.

It is worth stressing that microwaves, in contrast to conventional heating methods, are means of volumetric heating of materials (Fig. 2.1), which causes more extensive heating inside the material in comparison with outer layers of the material, which in turn makes hard a proper measurement of the reaction temperature. Moreover, as was described in

the other section (Section 3.5), temperature measurement under microwave conditions, particularly for the reactions in dense and solventless media, is difficult. Therefore, it source of inappropriate interpretation of experimental results and divergence in descriptions of the same experiments.

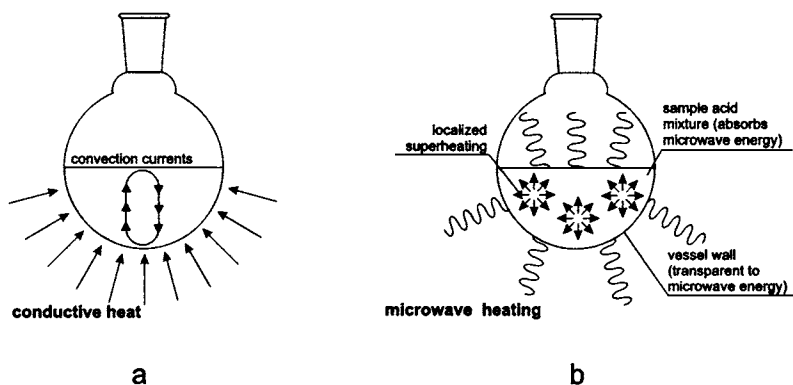


Figure 2.1. Different heating mechanisms for conventional and microwave heating.

### 2.1. Thermal activation during microwave irradiation

Thermal effects that reduce reaction times and which can be observed for the reactions under microwave irradiation are related to different temperature regime under microwave conditions in comparison to conventional conditions. However, they can result in a seemingly faster course of chemical reactions, the proper temperature measurement and its analysis for the entire sample of the material (i.e., the bulk reaction mixture) leads to the reaction rates that are comparable to reaction rates observed under conventional conditions. Three factors that can cause thermal effects are considered [3]:

- overheating (superheating) of the reaction mixture that in particular can be observed in the presence of a large quantity of electric carriers (i.e., ions)
- considerably faster heating rate of the reaction mixture which means that the required temperature for a chemical reaction is achieved in a shorter time
- increase of the rate of diffusive processes on the phase boundaries

Another important effect exhibited under microwave irradiation and caused by an overheating of the reaction mixture in sealed vessels is the so called "pressure cooker effect". For example, in one of the first published investigations, it was observed that a number of reactions can be carried out faster provided that the reaction mixtures were placed in sealed vessels and irradiated in a microwave cavity. Moreover, the reactions needed



even shorter reaction times if they were carried out in solvents with lower boiling points. Eventually, it was shown that the rates of the reactions were proportional to pressure developed in the reaction vessels during irradiation [12,8]. In another example, a reduction in reaction time was observed during the synthesis of organometallic compounds of rhodium(I) and iridium(I) that are usually prepared by boiling the reagents in a mixture of alcohols and water for several hours. The reaction time during the microwave protocol was shorter than 1 min. to afford products with satisfactory yield. Further more detailed investigation showed that the substantial reduction of the reaction time was attributed to the growth of pressure and temperature in sealed reaction vessels [19].

To avoid difficulties related to the growth of pressure in a sealed vessels as well as temperature measurement, the esterification reaction of acetic acid with propanol was carried out in an open vessel under reflux conditions. It was found that ester concentrations during the course of the reaction were comparable under both conventional and microwave conditions [20]. In a similar reaction (i.e., the esterification of trimethylbenzoic acid with propanol), the kinetic parameters of the reaction under the Arrhenius law were estimated for conventional conditions. Then ester concentrations were calculated theoretically and compared with the results obtained for the reaction under microwave conditions. It was found that the theoretical values correlated well with the experimental results so microwave irradiation did not influence the rate of the reaction [21].

In another approach, a high-boiling solvent, trichlorobenzene, was used for the investigation of the rate of Diels-Alder reaction of anthracene and diethyl fumarate. To estimate the temperature of under microwave irradiation, small capillary tubes containing compounds with diverse melting points were placed in the reaction mixture. The compound with the highest melting point that melted during the reaction described the reaction temperature. Then the reaction was repeated at the same temperature under conventional conditions. Again it was shown that microwaves did not influence the rate of the reaction and seemingly higher yields of the reaction under microwave conditions can be attributed to higher bulk temperature (a thermal effect) of the reaction mixture under microwave conditions [22]. Also comparison of the rate of Diels - Alder reaction of diethyl maleate and anthracene under conventional and microwave conditions gave similar results [21].

Study of the hydrolysis of adenosine triphosphate acid (ATP) showed that the temperature gradient during the reaction under microwave conditions can reach ca. 30°C , therefore reliable temperature measurement is the key factor for interpretation and comparison of rate of any reaction under conventional and microwave conditions. In this case, the Arrhenius parameters were estimated for the reaction under conventional conditions. Then taking into account the temperature gradient in investigated samples, the concentrations of the reagents were calculated for the experiments carried out under microwave conditions to show that both theoretical and experimental values fell within the range of the experimental error [23].

The microwave-assisted Biginelli synthesis of dihydropyrimidine was investigated in open vessels as well as sealed reaction vessels. The reaction carried out at atmospheric pressure under microwave irradiation in a solution showed no rate increase compared to

the reactions under conventional conditions, whereas under pressurized conditions the yield of the reaction even decreased and formation of various by-product was observed. The reaction rate enhancement was observed at atmospheric pressure in the case of superheating of the solvent (i.e., ethanol) even up to 116°C, but this effect can be rationalized as a pure thermal effect. More significant reaction rate and yield increase was observed when the solvent was allowed to rapidly evaporate and turn the reaction system into solvent-free systems [24], which by the way is one of the most efficient system for microwave activation.

All the mentioned above examples prove that for the investigated reactions the influence of microwave irradiation was limited to pure thermal effects (i.e., higher pressure and/or bulk temperature of the reaction mixture, development of temperature gradient, overheating of solvents) that can be responsible for seemingly higher reaction rates under microwave conditions. However, a careful consideration of all the factors that influence the reactions under microwave conditions can eliminate most of these effects, there are several of reactions in which the influence of only thermal effects do not sufficiently explain the enhancement of yield and rate of the reactions.

## 2.2. Non-thermal activation during microwave irradiation

Non-thermal microwave effects are often associated incorrectly with absorption of electromagnetic waves during rotational transitions of molecules (i.e., microwave spectroscopy), but the frequencies at which molecules can absorb electromagnetic waves to change their rotational states are higher than 2.45 GHz. For example, the first absorption lines of molecules such as OCS, CO, HF, and MeF occur at 12.2, 115, 1230 and 51 GHz, respectively. Moreover, molecular rotational spectra can be recorded only in the gas phase because in the condensed phase rotation of molecules is suppressed by neighboring molecules. Internal bond rotations referred to as torsional vibrations and oscillations in gas, liquid as well as solid states also require higher frequencies for excitation that falls into the infrared region. For instance, the excitation of molecules by infrared radiation at 100-400  $\text{cm}^{-1}$  requires frequencies at 3000-12000 GHz [25]. Thus, when the material absorbs microwave radiation at 2.45 GHz the increase of temperature is owing to macroscopic phenomena (e.g., dielectric heating mechanism), and this radiation does not bring molecules to higher rotational or vibrational energy levels. However, microwaves are converted into heat and quasi accumulated to increase internal energy of the material. It can be stated that microwaves "pump" energy into the material and due to the influence of accumulated thermal energy within the material it is possible to carry out a number of chemical reactions. Thus, it is considered that non-thermal microwave effects are due to such factors as:

- formation of *hot-spots* during the interaction of microwaves with the material
- increase in the transport of reagents within the reaction mixture; in particular, this is concerned with reactions under solvent-free conditions
- change of reaction selectivity due to increase in heating rate of the reaction mixture

- development and/or increase of dipole moment of the reacting molecules in the transition state compared to the ground state

In order to eliminate the influence of temperature on the rate of a chemical reaction, a reaction mixture of phthalic anhydride with amino acids was placed in a block of ice and then irradiated under microwave conditions. Ice was used to cool the reaction mixture because opposite to water it is transparent to microwaves ( $\epsilon'$  3.2,  $\epsilon''$  0.0029 at 25°C for 2.45 GHz) [26]. The reaction product was formed after 3 min. of irradiation while under conventional conditions the reaction was conducted in a boiling toluene solution for 1.5 h. However, since in such a case microwaves interact directly with the reaction mixture and temperature was not monitored during the experiments, it was stated that the increase of the reaction rate is not only due to thermal effects [27].

During the investigation of Diels-Alder reactions under microwave and conventional conditions was found that the bulk temperature of the reaction mixture is not representative because microwave irradiation led to the formation of a number of (*hot spots*) and caused the increase of reaction rate within their range [28]. Similarly, during the synthesis of long chain acetates under solvent-free conditions on mineral supports, it was stated that the 300-fold increase of reaction rate could not be explained only by an increase of the bulk temperature of the reaction mixture [10]. Eventually, the formation of "hot-spots" during microwave irradiation was proved during catalytic decomposition of  $H_2S$  in the gas phase on  $Al_2O_3$  support. These hot-spots were larger than 90  $\mu m$  and may be as large as 1000  $\mu m$  and have temperature 100-200°C above that of the remainder of the bulk. Such selective nature of the dielectric heating effect cannot be reproduced easily using conventional heating methods [29].

On the other hand, for the reactions under solvent-free conditions, diffusion of the reagents is the slowest stage that controls the reaction rate. Thus, every process that increases the diffusion rate can increase the overall reaction rate. To illustrate, it was found that in two different diffusive processes i.e., the diffusion of cations in glass [30], and the diffusion of ethylene oxide in poly(vinyl chloride) [31] microwave irradiation increases the diffusion processes in comparison to conventional heating, which can also explain the increase of the reaction rates under microwave irradiation for solvent-free conditions. Moreover, in a great number of experiments for the reaction under solvent-free phase-transfer catalysis (PTC), it was found that these reactions can be conducted under microwave irradiation without mechanical stirring of the reaction mixture to reach overall reaction rates even higher than under conventional conditions [32]. Reactions under PTC conditions usually require intensive mechanical stirring (ca. 800 rpm) to ensure high diffusion rates of the reagents at the phase boundary [33]. Therefore the increase of the diffusion rates on the phase boundaries for the reaction under solvent-free conditions can also explain the increase of the overall reaction rates that is not sufficiently explained by the temperature of the reaction mixture.

Since microwaves are the source of volumetric heating of materials which means that the temperature increase of the reaction mixture can be faster than for conventional heating methods (i.e., electric mantle, oil bath, etc.), it is possible to find a different product distribution (selectivity) under microwave and conventional conditions. For example, it

was shown that for the sulfonation of naphthalene in the presence of sulfuric acid [34], the rate of temperature growth of the reaction mixture influenced the ratio of the isomers 1- and 2-naphthalenesulfonic acid (1-, and 2-NSA). By changing the rate of temperature increase it was possible to have either kinetic or thermodynamic control of the reaction to obtain 1-NSA or 2-NSA, respectively. Furthermore, the ratio of the isomers of NSA did not depend on the heating mode (i.e., microwave or conventional) but only on the heating rate [35]. For reaction mixtures that are large in size (volume), it is possible to obtain the inversion of temperature pattern under microwave in comparison to conventional conditions (Fig. 2.2). This means that the material under microwave irradiation can have higher internal than outer temperature, which is different than bulk temperature of the reaction mixture. Therefore, it is possible to change selectivity or increase yield of reactions under microwave conditions, while the mechanism and kinetics of the reaction stay unchanged.

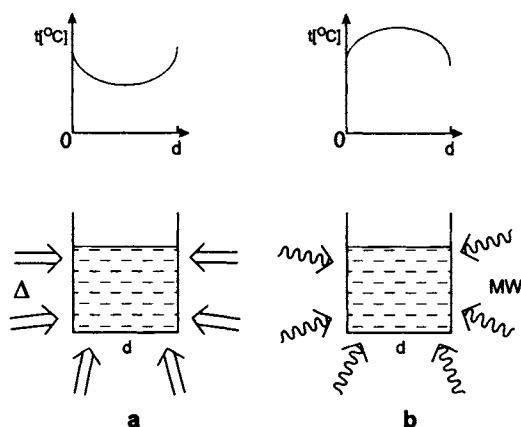


Figure 2.2. Temperature gradients for materials subjected either to (a) conventional heating or (b) microwave irradiation. Reprinted with the permission from [36].

Recently, it has been postulated that the increase of the polarity of the reaction system (i.e., either development or increase of dipole moment) from the ground state (GS) towards the transition state (TS) can result in an acceleration of the reaction due to a stronger interaction of microwaves with the reagents during the course of the reaction. Thus, non-thermal microwave effect can be expected for the reaction with polar mechanisms when the stabilization of the transition state (TS) is more effective than that of the ground state (GS), which results in an enhancement of the reactivity as a result of the decrease in activation energy (Fig. 2.3) [36].

The most representative examples of this are concerned with unimolecular or bimolecular reactions between neutral molecules (i.e., dipole moments are developed in the TS)

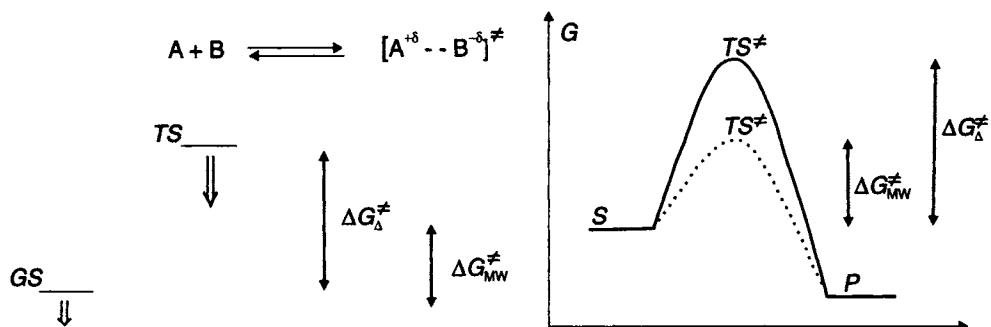


Figure 2.3. Relative stabilization of a more polar transition state (TS) when compared with the ground state (GS). Reprinted with the permission from [36].

and anionic reactions of tight ion pairs (i.e., charge localized anions) which leads to ionic dissociation in the TS [36].

All of these effects can be masked or limited by either protic (e.g., alcohols) or aprotic solvents (e.g. DMF,  $\text{CH}_3\text{CN}$ , DMSO) that strongly interact with and absorb of microwaves. In such cases the main interaction occurs between microwaves and polar molecules of the solvent which is used in an excess. Thus particularly for samples large in size, microwaves do not penetrate whole amount of the reaction mixture and a great amount of microwave energy is absorbed by the outer layers of the mixture (e.g., the penetration depth of water is ca. 1-2.5 cm, see Table 1.5). In turn, energy transport to the internal parts of the reaction mixture is by the classical heat conduction mechanism from the outer layers, which is commonly observed for conventional heating (Fig. 2.2). Therefore, reaction rates under microwave conditions in a polar solvent solution should be nearly the same as those observed under conventional conditions. However, this can lead to the conclusion that the most favorable systems for microwave activation are either non-polar or solvent-free systems, so the application of polar solvents should be always taken into account; in particular, for the reagents that are weak microwave absorbers, a polar solvent can initiate temperature rise of the reaction mixture - a small amount of a polar substance added to non-polar medium can dramatically improve microwave absorption as well as temperature homogeneity of the sample.

For example the efficiency of microwave absorption (i.e., amount of the microwave energy absorbed by a solution compared to the entire microwave energy emitted to the reactor cavity) was measured for n-hexane/2-propanol mixtures (Table 2.1). While pure n-hexane absorbs only little microwave energy, a mixture of 90 wt.-% n-hexane and 10 wt.-% 2-propanol clearly show a significant effect. Moreover, a mixture of 80 wt.-% n-hexane and 20 wt.-% 2-propanol already absorbs microwave radiation with an efficiency that is comparable of that of pure 2-propanol. As additional increase of the amount of 2-propanol does not lead to any further increase of efficiency [37].

Table 2.1

Efficiency of microwave irradiation at power input in 500 g of n-hexane and 2-propanol [37].

Solvent or mixture of solvents	Efficiency [%]
n-Hexane, pure	8
n-Hexane - 2-Propanol 9:1	50
n-Hexane - 2-Propanol 8:2	≥90
n-Hexane - 2-Propanol 7:3	≥90
n-Hexane - 2-Propanol 5:5	≥90
2-Propanol, pure	≥90

It should be stressed that the majority of literature reports on the acceleration of chemical reactions by microwave irradiation (even more than 1000 fold) come from the initial period of the application of microwaves in organic synthesis (i.e. from late 1980's and early 1980's). At this time there were no dedicated microwave scientific reactors available on the market, and most of these reactions were conducted in household microwave ovens. Recently, applying modern microwave reactors, scientists have verified a number of these reports, and it turns out that the claimed acceleration of the majority chemical reactions were attributed to difficulties with proper temperature measurements rather than to non-thermal microwave effects. Sometimes it was found that these effects were results of faster delivering of energy to the reaction systems [35,38].

It might seem that discussion of microwave effects should be already closed but more recently another series of papers have been published in which more accurate kinetic investigations suggest again that a fast rise of reaction temperatures does not explain differences between the rates of reactions under microwave and conventional conditions [16,18,39,40]. So we find a situation when after a short pause discussion revives again and becomes yet more interesting. However, it should be noted that there is difficult to find well documented examples in which a chemical reaction proceeds only under microwave conditions, while under conventional conditions no conversion of reagents is observed.

As was discussed above, the action of microwave irradiation on chemical reactions is still under debate, and a number of research groups have mentioned influence of thermal and/or non-thermal microwave effects on reaction rates. Regardless of the type of activation either thermal or non-thermal, microwave energy has its advantages which are still waiting to be fully understood and applied more widely for chemical processes. In our opinion, there are at least two factors that do not allow observing some effects that are related to non-thermal activation of chemical reactions under microwave conditions. To prove such non-thermal effects, accurate temperature control is needed together with kinetic examination of the reaction rate. First, the kinetic investigation of chemical reactions usually requires the use of dilute solution which is opposite to the reaction conditions that are most favorable for microwave activation i.e., dense and solvent-free solutions as well as heterogeneous systems. Second, detection of the bulk temperature of the reaction

mixture is most accurate in homogeneous and diluted solutions as well, so in case of dense or heterogeneous systems in which microwaves work most efficiently it is hard to tell the overall bulk temperature of the reaction mixture.

Nevertheless, a microwave effect would be very attractive from the point of chemists and would have an essential meaning for chemical synthesis, but first of all it would have far reasoning consequences for food industry. If it would shown that chemical processes under microwave irradiation are different from these occurring under conventional conditions, then this would put into question the utilization of microwave cookers in our everyday life. Therefore, the investigations into the effects on reactions run under microwave conditions are essential.

# Chapter 3

## Microwave equipment

Microwave reactors that are dedicated to carry out chemical syntheses are similar to other microwave systems and consist of a microwave power source (generator), section of transmission line (waveguide) that delivers microwaves from the generator into an applicator, and microwave applicator (cavity) (Fig. 3.1). The microwave applicator is the means by which microwaves can be efficiently coupled with the material. One of the frequently used applicators is a multimode microwave cavity the same as those used in microwave ovens. Other applicators in the form of horn antennae, radiators, and single-mode waveguide resonators can also be used to enable efficient coupling of the energy with the sample. A reliable measuring system is necessary to at least monitor temperature of the process, and for processes running at elevated pressures appropriate pressure control is required too.

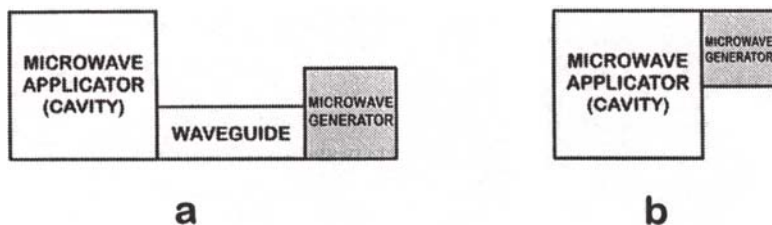


Figure 3.1. General schemes of microwave devices.

### 3.1. Microwave generators

The main types of microwave power sources are magnetrons and klystrons. Magnetrons which are commonly used in microwave ovens are mass produced thus cheap and easily available on the market. Therefore it is common practice to use the same magnetrons



for laboratory and industrial microwave processing. In general, magnetrons are vacuum devices consisting of an anode and a cathode, and the anode is kept at a higher potential than the cathode. As soon as the cathode is heated, electrons are emitted from it and are accelerated towards the anode by the electric field. At the same time, external magnets mounted around the magnetron anode block create the magnetic field parallel the axis of the cathode. This magnetic field forces the electrons to rotate around the cathode before they can reach the anode. The rotating electrons form a rotor moving around the cathode synchronously in the way that they deaccelerate and thus transform their energy into microwave oscillations in the cavities cut in the anode blocks. A typical anode block consists of an even number of small cavities that form a series of microwave circuits which are tuned to oscillate at a specified frequency dependently on the dimensions and shape of the cavities. Finally, microwave energy from one of the resonant cavities is coupled to the output transmission line, usually terminated with an output antenna (Fig. 3.2).

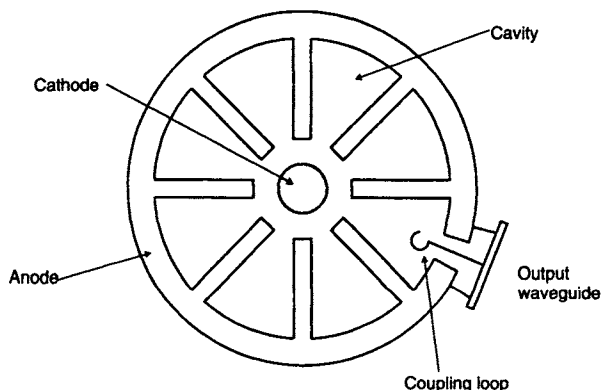


Figure 3.2. Schematic diagram of a magnetron shown in cross-section. Reprinted with the permission from [5].

In fact, magnetrons belong to a wider class of microwave devices which are called travelling wave tubes (TWT) with the difference that the magnetron has no input for microwaves and therefore can only be used as a generator, while a TWT can be used as an amplifier as well. This is because in a TWT an electron beam is moving along the so-called slow wave or travelling wave structure which can retard propagation of electromagnetic waves so they can conveniently (from the point of view of energy exchange) interact with and gain energy from the electrons moving in the same direction. Consequently, there is another type of microwave amplifier called backward wave tubes (BWT) in which the electrons and the wave travel in opposite directions. This can be more energy efficient for power sources in the submillimeter range of microwaves. An extensive description of microwave sources like travelling wave tubes (TWT), klystrons, disk-seal triodes and power grid tubes can be found in a number of books on industrial microwave applications

[5].

### 3.2. Transmission lines (waveguides)

Microwaves can be easily transmitted through various media. Hence, an applicator can be remote from the power source and connected to it via the transmission line, in which microwaves can be propagated using three types of modes. In transverse electromagnetic mode (TEM), all the components (i.e., magnetic and electric) are transverse which is similar if not an approximation of the radiation in free space. Both electric and magnetic components in the propagation direction ( $z$ ) are missing. Microwaves in TEM mode can propagate between two parallel wires, two parallel plates, or in coaxial lines, and are applied in general to low power systems ( $\leq 10$  kW) (Fig. 3.3)[5].

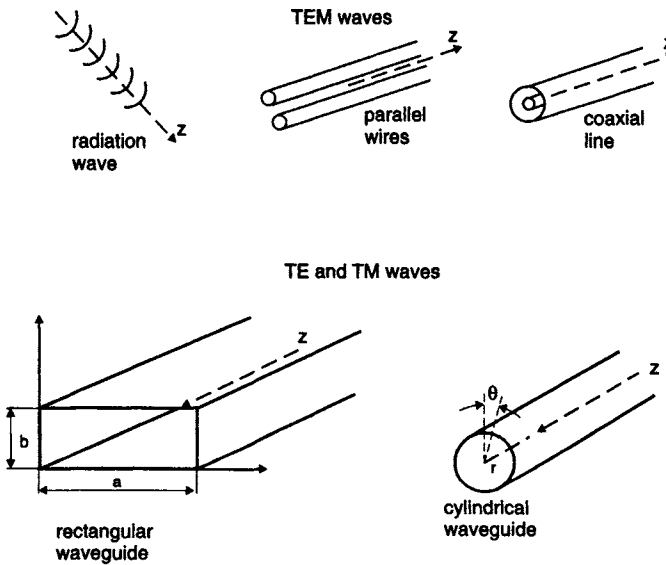


Figure 3.3. Waveguides for propagating transverse electromagnetic (TEM), transverse magnetic (TM), and transverse electric (TE) waves. Reprinted with the permission from [5].

The transverse electric (TE) and transverse magnetic (TM) are typical modes propagated inside metallic waveguides, which are basically hollow conducting pipes having either a rectangular or circular cross section. In the TE and TM mode, the component of the electric field and the magnetic field in the propagation direction is, respectively, missing. In general, every electromagnetic wave in rectangular or cylindrical waveguides can be described as a linear combination of the TE and TM modes, and, in turn, the

indexes in the propagation modes (e.g.,  $TE_{10}$ ) describe particular eigenvalues that define wave variation in a given direction. For example, a  $TE_{10}$  mode in rectangular waveguide specifies fundamental TE mode with one half-wavelength in the x-direction and zero half-wavelengths in the y-direction. If the waveguide section forms a cavity then a third index describes how many of half-wavelengths would fit along this section. For instance,  $TE_{103}$  is a cavity having one half-wavelength along x direction, 3 half-wavelengths along the z-direction and zero variation of electric field in y-direction (Fig. 3.4)[1].

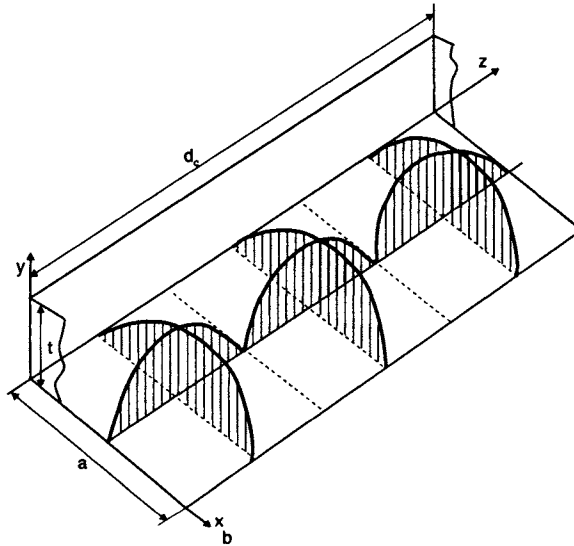


Figure 3.4. Development of standing waves:  $TE_{103}$  resonant cavity electric field pattern. Reprinted with the permission from [1].

### 3.3. Microwave applicators (cavities)

Microwave applicators may appear in many different shapes and dimensions and in fact their design is critical to processes run under microwave conditions since within applicators the microwave energy must be efficiently coupled to the material. A number of the most commonly used microwave applicators belong to three main types:

- multi-mode cavity
- single-mode cavity including TEM structures
- travelling wave applicators

The important criterion characterizing applicators is the maximum electrical field strength generated within the material. It is worth stressing that it is possible to map the field

strength distribution within a cavity by moving, for example, a small water load around it and recording the rate of temperature rise, but the results of such an exercise apply only to water. Once another target material is placed in the cavity, the field distribution is changed self-consistently.

The simplest applicator is a rectangular metal box that can accommodate the target material. While microwaves are applied into such a box via a waveguide, the microwaves undergo multiple reflections from the walls. The reflected waves interfere and, in so doing, their superposition establishes a distribution of electrical field strengths within the internal space (including the material), which within the band of frequencies covered by a magnetron corresponds to many different possible modes of oscillations. This reason such a metal box (cavity) is called a multi-mode microwave applicator (cavity) (Fig. 3.5). The most common example of this device is a cavity in domestic microwave oven usually with maximum microwave power less 1200 W and average power density in an empty cavity around 50 W/l (Table 3.1).

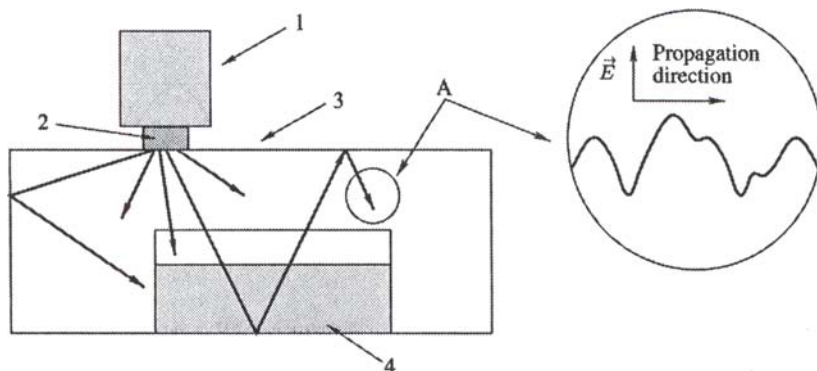


Figure 3.5. Multi-mode microwave reactor: 1 - magnetron, 2 - rotating deflector, 3 - multi-mode cavity, 4 - reaction vessel, A - non-regular shape of electromagnetic waves as a superposition of a number of waves.

The field distribution within the materials which is contained in a multi-mode applicator (cavity) depends not only on the real permittivity ( $\epsilon'$ ) and loss factor ( $\epsilon''$ ) of the material, but also on the size and location of the sample within the applicator. In this respect, a multi-mode device is best suited to a very lossy material occupying a relatively large volume (more than 50%) of the applicator. For low and medium loss materials occupying less than about 20% of the applicator volume, the temperature rise in the material, at best will be non uniform and at worst potentially damaging "hotspots" will occur as the result of extremely high local fields. However, by incorporating a mode stirrer (a rotating microwave deflector) and continuously rotating the material placed in the

applicator, temperature uniformity within the material can readily be improved. It must be underlined that multimode systems have a self-tuning feature i.e. they change field distribution and field strength dependently on the size, shape and absorption ability of the load. Disadvantageous in the use of a multi-mode applicators (cavities) for scientific studies is that since the spatial distribution of field strength is unknown, the possibility to generalize the results from a particular investigation is compromised, making it slightly difficult to attempt reliable reproducibility and as a consequence scaling-up the elaborated process.

By far a very efficient applicator, particularly for the syntheses on a small scale ( $\leq 50$  ml), is a single-mode resonant cavity, in which only one mode of microwave propagation is permitted and hence the field pattern is well defined so the material can be positioned accordingly (Fig. 3.6).

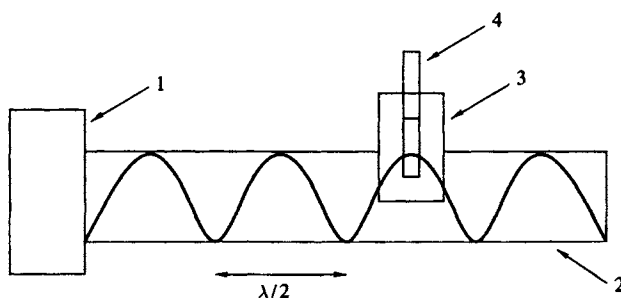


Figure 3.6. Single-mode microwave reactor: 1 - magnetron, 2 - waveguide, 3 - single-mode cavity, 4 - reaction vessel.

A single-mode cavity may be either cylindrical or rectangular, and the simplest (i.e., physically smallest) single-mode cavity operates in the  $TM_{010}$  mode in which the electrical field strength is constant along the main axis without variation of angle and is only a function of radius. The radius of the loaded cavity can be determined by solving the electric and magnetic field equations within the cavity under assumption of dimensions and particular boundary conditions. A rectangular single-mode cavity consists of a section of waveguide which is terminated with a non-contact plunger which in turn can tune the effective cavity length in order to obtain resonant frequency and conditions. The mode of operation of such a device is, typically,  $TE_{10}$  with the target material positioned in a region of high field strength. The major limitation of this device is that the length of the load (material) must be less than half a wavelength (ca. 6 cm for 2.45 GHz microwave frequency), otherwise the wave standing along the material would release heat in a periodic manner leading to a periodic heating pattern along the material. However, this can be overcome by e.g. moving the plunger or the material in a reciprocating fashion so that

the time-averaged field seen by the material is smoothed. Usually single-mode applicators (reactors) are characterized by maximum microwave power ca. 300 W but owing to much smaller size than multi-mode cavities the average power density of single-mode cavities can reach 1200 W/l (Table 3.1).

One of the solutions for the problems mentioned with the application of single- and multi-mode applicators (cavities) is the use of a travelling wave applicator (Fig. 3.7). However, it is not a common solution for the construction of microwave reactors. A travelling wave applicator consists of a section of a slow-wave structure with travelling wave propagating along it and coupled to the material in a spatially distributed manner. The wave is travelling, so enabling efficient coupling to a sample of the material having a bigger volume or larger surface than is passing through the structure, from the other end of which is launched a microwave source. As microwaves pass along the slow-wave structure they are absorbed by the material exponentially with distance and according to the dielectric properties and size of the sample. As a precaution in proper operation a dummy water load is attached to load-end of the waveguide to absorb the residue of microwave energy which was not absorbed by the material. Provided that the load can move at a constant speed along the structure, each part of it would experience the same total field strength once steady state conditions are achieved i.e. after at least one length of material has already passed through the structure.

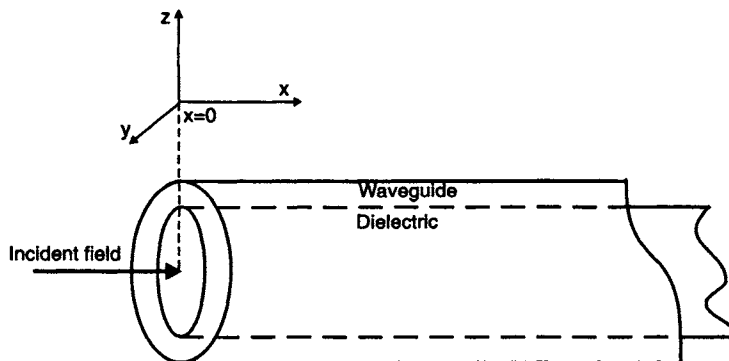


Figure 3.7. Travelling wave applicator.

### 3.4. Microwave reactors

In the literature, first microwave-assisted experiments on organic synthesis employed multimode household microwave ovens [12,13]. More recently, the use of microwave reactors for chemical syntheses has become more advanced, and, at the moment, some chemical journals specializing in organic chemistry intend to refuse manuscripts in which experiments were carried out in a domestic microwave oven (even including ovens with

modifications). Nevertheless, the main advantage of household microwave ovens is their low cost compared to commercially available microwave reactors and often the possibility to adjust such ovens for chemical synthesis by drilling shielded (!) outlets in the oven walls for assembling appropriate elements such as an upright condenser, stirrer, dropping funnel, etc. (Fig. 3.8). However, all of these modifications have to be performed by professional services specializing in microwave equipments.

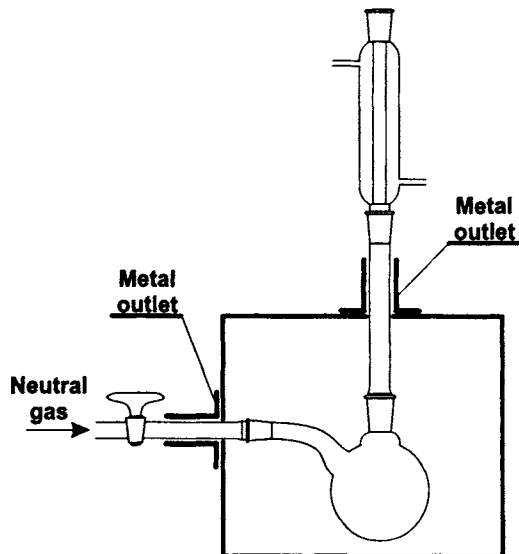


Figure 3.8. Modification of a microwave cavity for performing chemical reactions under reflux conditions.

The main disadvantage of domestic microwave ovens is a pulsating-mode duty cycle to effect adjustable power regulation. Such regulation, typical for both cheap and expensive household microwave ovens has the feature that variable power is always obtained by switching off and on the magnetron i.e. using a fixed power at a variable time base. However, some domestic ovens can well be suited to carry out a number of organic syntheses provided that adequate safety precautions are undertaken. Although some readers might not have experience in application of microwaves, for the purpose of this book all the experiments with chemical reactions described in this book have been carried out using specialized, commercially available microwave reactors.

Specialized microwave reactors for chemical synthesis are commercially available from several companies: Anthon-Paar [41], Biotage [42], CEM [43], Ertec [44], Lambda Technologies [45], Microwave Materials Technologies (MMT), Milestone [46], and Plazmatron-ika [47]. They offer a number of multi-mode and single-mode reactors which are mostly

adopted from microwave multi-mode cavities and single-mode systems developed for digestion of analytical samples, respectively. The reactors can be equipped with built-in magnetic stirrer and direct temperature control by means of an IR pyrometer, shielded thermocouple or fiber-optical temperature sensor, and continuous power feedback control, which enable heating of a reaction mixture to a desired temperature without thermal run-aways. In some cases, it is possible to work under a reduced pressure or under pressurized conditions within the cavity or in reaction vessels. The comparison of different type of microwave reactors with a household microwave oven (i.e., Sharp R-220A) is given in Table 3.1 [37].

Table 3.1

Comparison of different microwave systems [37].

Parameters	Microwave R-220A (Sharp)	Synthwave 402 (Prolabo CEM)	Ethos MR Milestone
Microwave mode	multi-mode	single-mode	multi-mode
Microwave power	800 W, pulsed	300 W, unpulsed	1000 W, pulsed/ unpulsed
Volume of cavity	15.7 dm <sup>3</sup>	≤ 0.25 dm <sup>3</sup>	42.8 dm <sup>3</sup>
Power density	approx. 50 W/dm <sup>3</sup>	≤ 1200 W/dm <sup>3</sup>	approx. 23 W/dm <sup>3</sup>
Reaction scale	≤ 100 g (dry reaction)	≤ 100g	up to 3000 g (depending on reactor type)

In fact, the strict distinctions between multi-mode and single-mode systems can be misleading in laboratory practice. For instance, in single-mode cavities the material is irradiated only from one side and, in particular, for the systems with high power density (around 300 W/L), electrical as well as temperature inhomogeneities are observed. Furthermore, vessels with diverse reaction mixtures inside the single-mode cavity influence the field geometry, and new modes of microwaves may be created by reflections and subsequent interferences, which eventually may result in a two- or three-mode system. Therefore, from a practical point of view, it seems to be better to follow the rule that batch reactions on a scale higher than 50 ml should be performed in multi-mode microwave reactors while the reactions on a scale lower than 10 ml should be carried out in single-mode reactors. Unfortunately, the typical region for chemical syntheses performed in the laboratory is often in the range of 10 to 50 ml, so we have to leave to the experience of the chemist to assess the kind of materials in his hands and choose type of microwave cavity. Even a small amount of the material that is a good microwave absorber can be very efficiently heated in single- as well as multi-mode cavities. Nevertheless, in multi-mode reactors (cavities) it is difficult to obtain high radiation intensities (power densities) within small samples of materials because usually the cavity is much larger in size than the sample. In such a case only a small part of the microwave radiation is absorbed by



the sample when the rest of radiation is dissipated and converted into heat on the walls of the cavity. On the other hand, in single-mode cavities, the amount of the material is limited by the size of the cavities which have to be smaller than half a wavelength, which is ca. 6 cm for 2.45 GHz microwave frequency, otherwise the samples are heated unevenly resulting in at temperature inhomogeneities; particularly for systems with high average power densities.

The reader should be also aware that a number of commercially available systems for high-throughput as well as combinatorial chemistry have recently been provided by microwave equipment manufacturers, but their description is out of the scope of this book. Extensive descriptions of such systems can be found in recently publish books [32,48].

### 3.5. Temperature monitoring

As was mentioned above, every efficient application of microwave energy to perform chemical syntheses requires reliable temperature measurement as well as continuous power feedback control, which enable heating of reaction mixtures to a desired temperature without thermal runaways. Moreover, power feedback control systems that are operated in the most microwave reactors enable a synthesis to be carried out without knowing the dielectric properties or/and conductive properties of all the components of the reaction mixture in detail. On the other hand, temperature control during microwave irradiation is a major problem that one faces during microwave-assisted chemical reactions. In general, temperature in microwave field can be measured by means of:

- fiber-optic thermometer
- shielded thermocouple
- pyrometer (IR sensor)

Fiber-optic thermometers can be applied up to 300°C , but are too fragile for real industrial applications. In turn, optical pyrometers and thermocouples can be used, but pyrometers measure only surface temperatures which in fact can be lower than the interior temperatures in reaction mixtures. Application of thermocouples which in case of microwaves are metallic probes, screened against microwaves, can result in arcing between the thermocouple shield and the cavity walls leading to failures in thermocouple performance.

The temperature of microwave irradiated samples can be also measured by inserting either a thermocouple or thermometer into the hot material immediately after turning off microwave power. This rather simple procedure may sometimes help if no other means of temperature measurements is provided. However, it must be stressed that the temperature of many materials can drop quickly as soon as microwave power is switched off.

## Chapter 4

# Reaction vessels and glassware

In many cases choice of the reaction vessel in which the synthesis under microwave condition is planned to be carried out depends on the type of microwave cavity (reactor) that is available in the laboratory. In turn, as was mentioned in the Section 3.4, the choice of microwave reactor (i.e., single- or multi-mode system if it is possible to choose between them) depends on the volume of the reaction mixture. It can happen that in a multi-mode reactor it can be difficult to obtain high radiation intensity (power density) within small samples, since usually the cavity is much larger in size than the sample. In such a case, the reaction mixture does not absorb enough energy to initiate the reaction because only a small part of the microwave radiation is absorbed by the reaction mixture when the rest of radiation is dissipated and converted into heat on the walls of the cavity. On the other hand, in single-mode reactors that are characterized by much higher power density (Table 3.4), the amount of the reagents is limited by the small size of such cavities, and the diameter of the reaction vessels have to be equal or smaller than half of the wavelength, which for the frequency of 2.45 GHz is ca. 6 cm.

In this book, the reaction vessels most often prescribed for reaction procedures in multimode reactors consists of a round-bottomed flask with one or two vertical necks that can be provided with an upright condenser, dropping funnel, neutral gas inlet, and fiber-optical thermometer. Depending on the type of additional equipment, all of these pieces can be connected with the flask through a long-neck adapter (tube) that goes through the specially shielded inlet situated on the top of the microwave cavity (Fig. 3.8). It must be stressed again that such inlets must be shielded by specially designed metal tubes in order to prevent leakage from the microwave cavity, and under any conditions the inlets cannot be removed from microwave reactors. It is unnecessary and even possible to apply flasks with more than two necks in multi-mode microwave reactors, since the upright condenser can be combined with the dropping funnel and gas inlet (Fig. 4.1). Moreover, most of the multimode reactors are equipped with efficient magnetic stirrers as well as either fiber-optic or infrared temperature detections. In some cases, the reaction mixture consists only of solids and high boiling liquids (e.g., neat reaction or solventless conditions) thus it is not necessary to use an upright condenser; however, a long-neck adapter has to be always placed on the flask to prevent both the reaction mixture from sparks generated in

the microwave cavity as well as to protect the microwave cavity from vapors generated within the reaction mixture (Fig. 4.1) (see also Section 6).

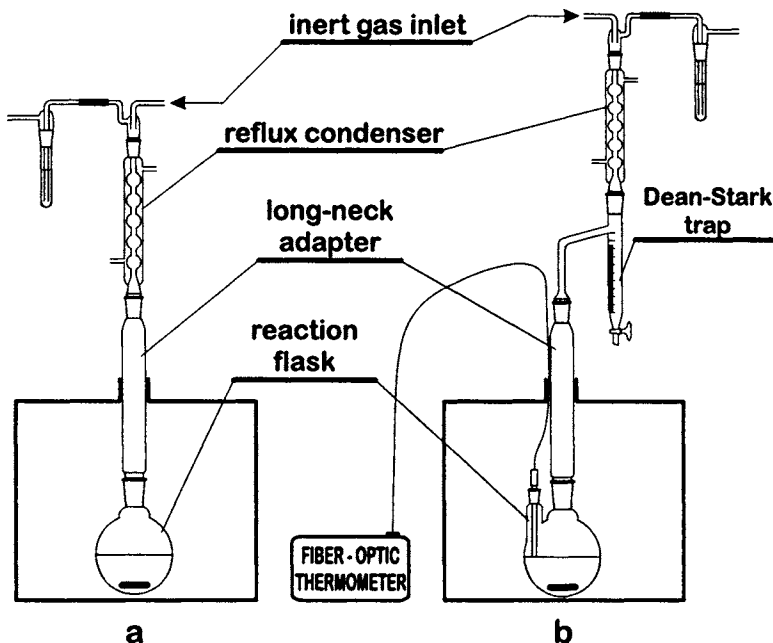


Figure 4.1. Experimental set-up for reactions in multi-mode microwave reactors.

Although in a number of publications on microwave-assisted synthesis the use of glassware made of quartz is strongly advocated because of its transparency to microwave irradiation, in laboratory practice quartz vessels can be substituted with less fragile and cheaper borosilicate glass (e.g., Pyrex) vessels with ground glass joints. Since borosilicate glassware is commonly used in laboratory practice, it can be expected that any reaction performed under atmospheric pressure with the usage of typical laboratory glass components is easy to configure and transfer to work inside multimode microwave reactors (cavities). All the reactions take place inside the cavity so the chemistry is processed safely and securely inside its steel walls. It is much more important to avoid the use of metal clamps and material that strongly absorb microwave energy to connect glassware within the microwave cavity. Pieces of metal can cause arching and sparking in the cavity while pieces of material (e.g., black rubber) that absorb microwaves can be damaged and even catch fire. Thus, Teflon joints are more advocated than, for example, rubber joints (see Section 6). Moreover, typical magnetic stir bars that are usually coated with Teflon can be used so as not to cause any problem in the vessels introduced into the microwave reactors provided that the reactor is equipped with a magnetic stirrer.

Reactions under pressurized conditions are not illustrated in this book, although there are a number of pressurized reaction vessels made of ceramic and plastic materials provided by the manufactures of microwave equipment (see Section 3.4). These vessels should not be replaced under any conditions with other vessels and cannot be switched between different type of microwave reactors either.

For reactions that are planned to be carried out in single-mode reactors there is available a great number of differently shaped vessels usually provided by the producers of microwave equipments (see Section 3.4). These vessels, which can be also made of borosilicate glass as was mentioned in the previous paragraph, have different diameters depending on their intended volume (Fig. 4.2).

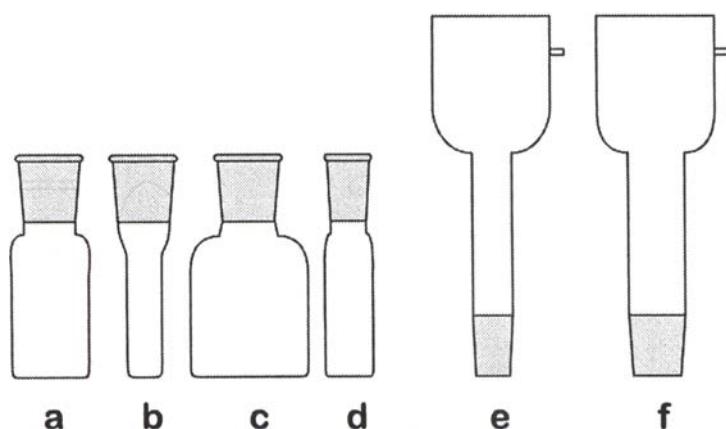


Figure 4.2. Reaction vessels and adapters for reactions in single-mode microwave reactors (a) - 60 cm<sup>3</sup>, (b) - 25 cm<sup>3</sup>, (c) - 90 cm<sup>3</sup>, (d) - 30 cm<sup>3</sup>.

In order to absorb as much of microwave energy as possible, the volume of the reaction vessels should be large enough to keep the entire sample of the material within the microwave cavity but also small enough to not keep the reaction mixture as only a layer at the bottom of the reaction vessel (Fig. 4.3a). From the experience of the author of the book, the best results can be achieved if the part of the reaction vessel immersed in the microwave cavity is from 30 to 75% filled with the reaction mixture (Fig. 4.3c).

Similarly to the reaction in multi-mode cavities, a long-neck adapter (tube) can be placed on top of the reaction vessel in order to connect it with additional pieces of equipments such as a cold finger, dropping funnel, neutral gas inlet, and fiber-optical thermometer. However, in the opposite to multi-mode reactors, the reaction flask together with long-neck adapter is placed additionally in a quartz cylinder to prevent the reactor from damage in case of any breakage of the reaction flask. Since according to some designs of single-mode microwave reactors, the reaction vessels are rotated in order to obtain

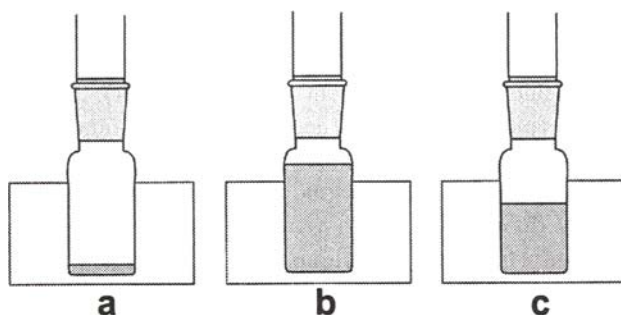


Figure 4.3. Volume of reaction mixtures during experiments in single-mode reactors: (a) - volume of the reaction vessel is too big, (b) - volume of the reaction vessel is too small, (c) - volume of the reaction vessel is correct.

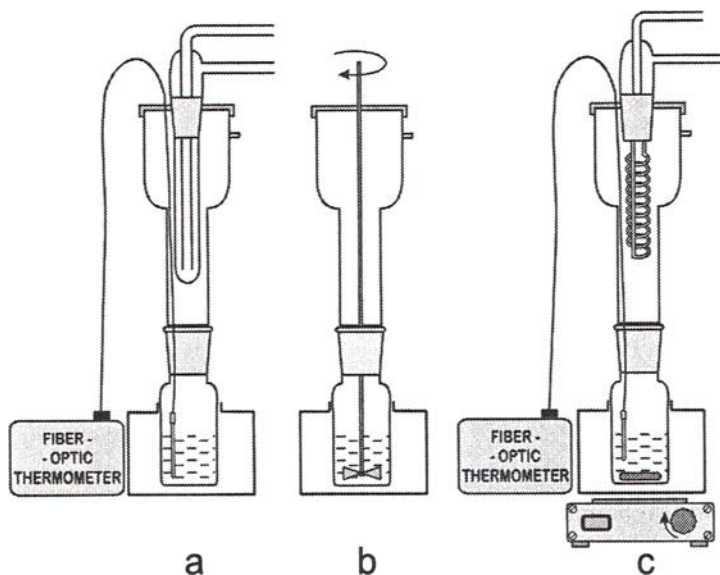


Figure 4.4. Experimental set-up for reactions in single-mode microwave reactors.

more uniform irradiation at the reaction vessels, it is recommended to use a cold finger rather than an upright condenser because of greater simplicity of such a setup. Nevertheless, an upright condenser can be used if the reactor is equipped with a magnetic stirrer. Some typical setups for the reactions with the use of single-mode systems (reactors) are illustrated in Figure 4.4.

For both type of microwave reactors, if the reactor is not supplied with a temperature sensor or more likely accurate temperature measurement is prerequisite during an experiment, the fiber-optic temperature sensor is directly applied to the reaction mixture. In order to secure the sensor from harsh chemicals, the sensor is inserted into a capillary that in turn is inserted into the reaction mixture. In such a case, it is strongly advocated to use capillaries that are made of quartz glass and are transparent to microwave irradiation. Any capillary that is made of glass or even borosilicate glass can always slightly absorb microwave energy, in particular, while the reaction mixture does not absorb microwaves efficiently, and in turn lead to failures of fiber-optic thermometer performance.

However, such reactions are not exemplified in this book. There is also a great number of single-mode reaction systems with automated feeder of the reaction vessels provided by the microwave equipment manufactures, but the description of these systems is out of the scope of this book. The description of such system can be found in recently published books [32,48].

## Chapter 5

# Techniques for conducting chemical reactions under microwave irradiation.

Two pioneering works that were published almost 20-years ago [12,13] described several organic syntheses that were completed in high yield when conducted in domestic microwave ovens in sealed glass or Teflon vessels. Since then different techniques have been developed and they are presented here in order to allow readers to choose the most appropriate techniques for their needs.

The simplest method for conducting microwave-assisted reactions involves irradiation of reactants in an open vessel. During the reaction, reactants are in a solution of a polar high-boiling solvent so that the temperature of the reaction mixture does not reach the boiling point of the solvent. Such a method was termed "Microwave-Organic Reaction Enhancement" (MORE) [49]. Despite the convenience, a disadvantage of the MORE technique consists in the limitation to high-boiling polar solvents such as DMSO, DMF, N-methylmorpholine, diglyme etc. This approach has been adapted to lower-boiling solvents (e.g. toluene) and reflux conditions, but, for reactions at reflux, microwave cavities (reactors) have to be modified, e.g. by making a shielded opening to prevent the leakage of microwaves, through which the reaction vessel has to be connected to an upright condenser, dropping funnel, neutral gas inlet, etc. A number of reflux systems have been developed in an effort to use solvents in microwave-assisted synthesis without the risk of explosion. The most important feature of such reactors is to prevent flammable vapors escaping from a microwave cavity (applicator), in which the generation of electric arcs created from interaction of microwaves with such materials as small pieces of metals, graphite, etc constitutes a potential hazard of an explosion.

As was mentioned previously, pressurized conditions have been reported for microwave-assisted organic synthesis [50]. The reactions were carried out at a domestic microwave oven and commercially available screw-up pressure vessels made of Teflon, PET and PEEK, which are both microwave transparent (Fig. 5.1). It has to be pointed out that reactions under such conditions have to be strictly controlled with an efficient power feed-

back because any vessel can become over-pressurized resulting in a danger of explosions. Fortunately, most microwave reactors are nowadays equipped with a direct temperature and pressure control, which in turn avoids failures owing to thermal and pressure runaways of chemical reactions. This strategy has been successfully applied to a great number of syntheses, but one needs to keep in mind that it always generates a risk of explosions if the equipment is not operated properly.

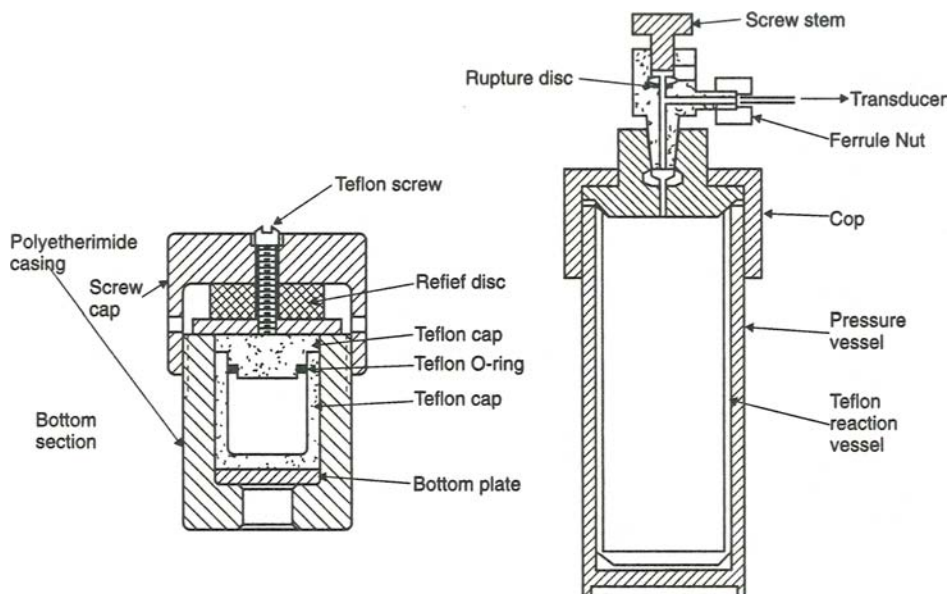


Figure 5.1. Reaction vessels for performing chemical reactions under pressurized conditions. Reprinted with the permission from [3].

Microwave heating has proven to be of benefit particularly for reactions under "dry" media (e.g., solvent-free conditions) in open vessel systems (i.e., in the absence of a solvent, on solid support with or without catalysts) [4]. Reactions under "dry" conditions were originally developed in the late 1980's [51], but solventless systems under microwave conditions offer several additional advantages. The absence of solvent reduces the risk of explosions when the reaction takes place in a closed vessel. Moreover, aprotic dipolar solvents with high boiling points are expensive and difficult to remove from the reaction mixtures. During microwave induction of reactions under dry conditions, the reactants adsorbed on the surface of alumina, silica gel, clay, and other mineral supports absorb microwaves whereas the support does not, and transmission of microwaves is not restricted. Moreover, microwaves can interact directly with reagents and, therefore, can more efficiently drive chemical reactions. The possible accelerations of such reactions are expected



to be optimal since they are not moderate or impeded by solvents. Consequently, such supported reagents efficiently induce reactions under safe and simple conditions even with domestic microwave ovens instead of expensive specialized commercial microwave systems. Applying solvent-free conditions, three general possibilities can be realized [52]:

- reagent supported on mineral oxides and/or graphite
- solid-liquid solvent-free phase transfer catalysis (PTC)
- neat reaction

Aluminas, silicas, clays, zeolites or graphite can be selected as acidic, basic or neutral supports, depending on the type of reactions. Alumina alone can act as a base towards acid compounds but if a strong base is necessary, KF on alumina can ionize carbon acids up to  $pK_a = 35$ . On the other hand, montmorillonites (clays) such as K10 or KSF offer acidities very comparable to strong mineral acids (e.g., nitric and sulfuric acids, respectively). Reactions are simply performed by mixing reagents and a mineral support in the absence of any organic solvent followed by microwave irradiation [52].

Phase-transfer catalytic (PTC) conditions, which are specific for anionic reactions (and anionic activation) are perfectly well tailored for microwave activation, because after ion exchange between a substrate and catalyst, the resulting nucleophilic ion pair is a highly polar species especially prone to interaction with microwaves [32]. Eventually, the mixture of neat reagents in an open vessel can lead to a reaction under microwave conditions provided that one of the reagents is liquid or a low melting solid that couples well with microwaves. On the other hand, even a small amount of a good microwave absorber (e.g.,  $H_2O$ ,  $DMF$ ; for example, see Table 1.3) added to reaction mixtures that consist of substrates that do not absorb microwaves in the solid state can initiate an increase of reaction mixture temperature and then chemical reaction.

In general, reactions under solvent-free conditions performed in a dense media suffer difficulties with heat transfer through the reaction medium and homogenous heating under conventional conditions. Since microwave irradiation is a means of volumetric heating of materials, temperature is more uniformly distributed under microwave conditions. Improvement of temperature homogeneity and heating rate implies, in turn, faster reactions and less degradation of the final products. For the purpose of this book and taking into account some safety precautions, all the experiments performed and described here have been carried out in open vessels, sometime under reflux conditions. Therefore, four reaction systems were chosen to carry out the synthesis under microwave conditions, and the reactions are grouped according to these systems, i.e.:

- reactions in homogenous media
- reactions of reagents supported on mineral supports
- solid-liquid solvent-free phase transfer catalysis (PTC) reactions
- reactions of neat reagents

More extensive description of the methods for performing chemical reactions under microwave irradiation can be found in recently published books [32,48].

## Chapter 6

# Safety precautions on the application of microwaves in laboratory

Considering synthesis under microwave conditions, microwave reactors and ovens used in the laboratory may pose several different types of hazards. Therefore, the chemists are obliged to accept a unique set of precautions (usually given by the manufacturer of the microwave equipment) in addition to those of good practice and common behavior in the chemistry laboratory. Microwaves are absorbed not only by organic solvents, reactants, catalysts, and their supports to carry out chemical reactions but also are absorbed by reaction vessels, materials, surfaces of equipments that are not intended to be heated during reactions. Moreover, microwaves at the frequency range of 2.45 GHz and 915 MHz are also absorbed by human tissue. They penetrate (penetration depth  $D_p$ : 2.0 and 3.0 cm, respectively) and can raise the temperature of tissue and blood, which can result in overheating and serious danger. Therefore, all the microwave equipment as well as microwave reactors designed to be used in laboratories are shielded to prevent the operators from such exposure. Most industrial countries have established safety standards and limits for microwave radiation exposure. For example, in the United States microwave energy exposure from laboratory and domestic equipment at 2.45 GHz is limited to 5 mW/cm<sup>2</sup> at a distance of 5 cm from the equipment surface.

Most microwave equipment available on the market is designed and constructed in such a way to reduce leakage of microwaves from any part of the equipment to below required limits. This is realized by building a magnetron tube and microwave cavity within continuous metal housing covering their interior. The door (viewing) window contains a metal grid with small holes through which light can pass but microwaves are prevented from passing. The equipment has at least one interlock switch used to prevent accidental exposure by turning off emission of microwave energy into the microwave cavity if the microwave system door is open. Safety devices should never be removed from any microwave equipment. For example, the metal grid is removed from the door (viewing), then the plastic window becomes transparent to microwave radiation, which can be transmitted into the laboratory.

However, all these designs tend to make microwave equipment extremely safe during

normal use, a proper usage of laboratory microwave equipment is the responsibility of the operators. Therefore, all the components important for safe operation should be inspected for damage and leakage to ensure that the equipment is maintained in safe working order. It must be stressed here again that any modification of microwave equipment to adopt it for a new intended use, such as a converting household microwave oven for laboratory use, should be conducted by professional services that specialize in the fabrication of microwave equipments and who understand the shielding requirements. It is also highly advisable to contact the manufacturers about proposed modifications.

Even though in some cases the original works given in the references have been conducted in household microwave ovens, all the experiments presented in the book have been carried out in the dedicated microwave reactors (see Section 3.4), which can result in differences in reaction temperatures and times while compared to the original references.

User safety in case of unforeseen spontaneous reaction is one of the major concerns in microwave-assisted chemistry. In general, most of laboratory equipment is built for conducting specific but well defined reactions or to study a group of reactions. In contrast, microwave reactors are general-purpose systems where reaction conditions are not specified and often unknown to designers and manufactures. Moreover, energy transfer within microwave vessels is via direct absorption by solvents, substrates, or/and reactants, and in particular for exothermic reactions the temperature of the reaction mixture can rise rapidly. In such a case, a temperature control device may stop further microwave irradiation when the reaction temperature is reached, but if there is no effective cooling of the reaction vessels the heat generated during the reaction may cause further spontaneous temperature increase even to uncontrollable level. However, this is of the utmost importance for reactions in closed vessels, whereas in the case of the reaction in open vessels, the reaction temperature may largely exceed the boiling points of the reaction components, which can throw the reaction mixture from the vessel.

Use of organic flammable solvents and reactants can generate other potential hazardous conditions that can be foreseen during microwave-assisted synthesis. Depended on the equipment, sparks and arching from magnetrons, metal elements of the microwave cavity as well as metal elements and other pieces like graphite, metal powder inserted either intentionally or unintentionally to a microwave cavity are common. Therefore, most microwave reactors are equipped with an organic solvent sensor to terminate power to the magnetron and microwave irradiation if the flammable vapors are detected. Obviously, the vapours must be cleared from the reactor cavity before restarting the reactor. If a reactor is not equipped with a vapor sensor, the solution for the reaction in an open vessel under microwave conditions is to assemble with the reaction vessel a long-neck adapter (tube) that connects the vessel with an upright condenser outside of the microwave cavity (Fig. 3.8). In such a case, small amounts of vapors that can penetrate the vessel and adapter joints are removed from the reactor cavity by an internal fan system. Hence, placing a microwave reactor inside a fume hood, where exhausted vapor solvents may get circulated around the unit is also highly advisable. Moreover, as was mentioned earlier, it is also important to avoid the use of metal elements and material that strongly absorbed

microwave energy to connect glassware within the microwave cavity (see Section 4.2). It is a good laboratory practice to check properties of the material that is intended to be used for joints. If no data are available in the literature, do NOT use it. In a number of cases, it is difficult to find appropriate data in the literature on the dielectric properties of different materials. Thus, if the material is intended to be used as a joint, seal, etc., it should be placed in the microwave cavity and irradiated with moderate power for a short time. If the material gets warm, it should be never used as a joint nor seal. In the experiments performed in this book, when it is necessary only Teflon joints are used.

The evaluation of the unsafe conditions and practices that may occur in the chemical laboratory related to operation of microwave systems together with case studies and mechanism for periodic updating of safety information, including the capability for microwave systems users to input their own contributions has been provided in more detail [53]. Whereas more general rules on operating microwave cavities in the laboratory to minimize the risk of hazards can be found on the webpage of NIEHS (Courtesy of Health and Safety Branch, National Institute of Environmental Health Sciences, National Institutes of Health [54]).

### **Operating microwave ovens in the laboratory:**

1. Do not operate the oven if it is damaged. It is very important that the oven door close properly and that there is no damage to the door seals and sealing surfaces, hinges and latches.
2. Since there may be residual contamination, never use the laboratory microwave oven to heat food or drinks. Institute policy and federal regulations do not allow these items consumed or stored in the laboratory.
3. Do not use the microwave oven to heat up hazardous chemicals or radioactive materials.
4. Do not use ALUMINUM FOIL at anytime during the heating cycle. Metal utensils and utensils with metallic trim should not be used in the microwave oven.
5. Avoid heating materials in cylindrical-shaped containers. Liquids heated in certain shaped containers (especially cylindrical-shaped containers) may become overheated. When overheated, liquids may splatter during or after the heating cycle resulting in possible employee injury or damage to the microwave oven.
6. When heating liquids in screw-cap bottles, completely loosen the screw-caps to prevent pressure build-up within the container. This pressure build-up with a cap that is not sufficiently loose can cause the bottle to explode.
7. If steam accumulates inside or outside of the oven door, wipe with a soft cloth. This may occur when the microwave oven is operated under high humidity conditions and in no way indicates malfunction of the unit.

8. Be careful when removing containers from the microwave. Some containers absorb heat and may be very hot. Always use protective gloves and appropriate eye/face protection to minimize any possible injuries.
9. If materials inside the oven should ignite, **KEEP OVEN DOOR CLOSED**, turn oven off, and disconnect the power cord.
10. Do not attempt to tamper with or make any adjustments or repairs to door control panel, safety interlock switches or any other part of the oven. Repairs should be done by qualified service personnel only.

## Chapter 7

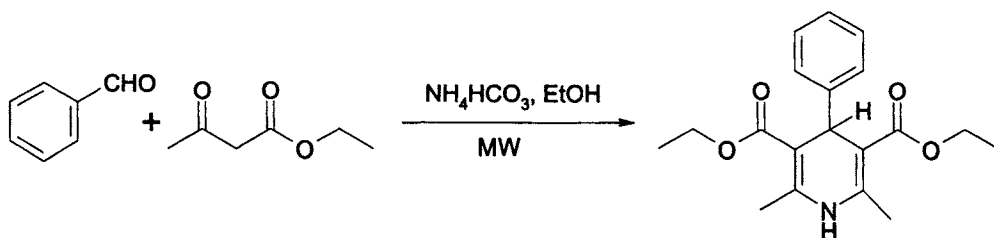
# Reactions under microwave conditions

Some information on hazards related to chemicals and solvents that are used in the book is listed together with the preparation procedures and in the appendix. However, the list is not exhaustive and the reader is referred to other sources (e.g., [55,56]). The description of a number of techniques that are used in organic laboratory during for analysis, separation, and purification of organic compounds is out of the scope of this book. Therefore, the reader is referred to some excellent textbooks on practical organic chemistry (e.g. [57,58]).

### 7.1. Reactions in homogenous media and solvent

#### 7.1.1. 2,6-Dimethyl-4-phenyl-1,4-dihydro-pyridine-3,5-dicarboxylic acid diethyl ester

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

Benzaldehyde	2.12 g, 19 mmol	eye irritant, harmful by inhalation or ingestion, may be harmful by skin contact and cause allergic reaction
Ethyl acetoacetate	5.72 g, 40 mmol	severe eye irritant, mucous mebrane and respiratory irritant, may be harmful by inhalation
Ammonium bicarbonate	1.98 g, 25 mmol	may irritate eyes
Ethanol	6 ml	causes skin and eye irritation

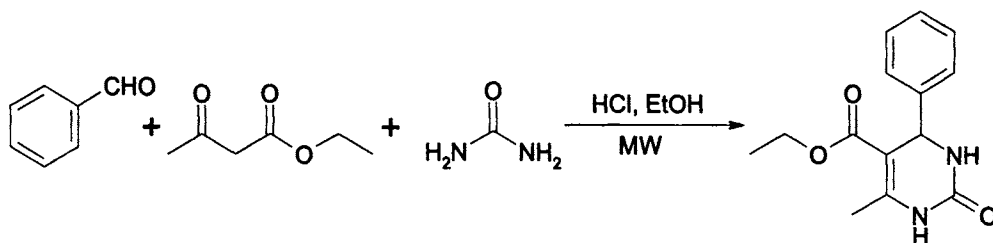
**Method [37]**

1. To a clean reaction vessel add ethanol (6 ml), benzaldehyde (2.12 g, 19 mmol), ethyl acetoacetate (5.72 g, 40 mmol), ammonium bicarbonate (1.98 g, 25 mmol)
2. Stir the mixture for 10-20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 30 min. so that ethanol reflux during the irradiation.
5. Allow the reaction mixture to cool to room temperature, concentrate the solution by rotary evaporation and recrystallize the product from ethanol; m.p. 154-156°C , yield > 80%.



### 7.1.2. 6-Methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

#### Materials

Benzaldehyde 2.22 g, 20 mmol

Ethyl acetoacetate 2.60 g, 20 mmol

Urea 1.44 g, 20 mmol

Hydrochloric acid 0.023 g,  $6.5 \cdot 10^{-4}$  mmol  
(36 %)

Ethanol 6 ml

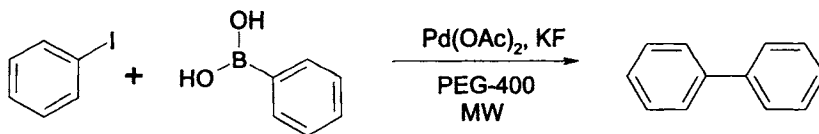
eye irritant, harmful by inhalation or ingestion, may be harmful by skin contact and cause allergic reaction  
severe eye irritant, mucous mebrane and respiratory irritant, may be harmful by inhalation irritant, prolonged exposure may cause allergic reaction in some individuals  
extremely corrosive, inhalation of vapour can cause serious injury, ingestion may be fatal, liquid can cause severe damage to skin and eyes  
causes skin and eye irritation

**Method [24]**

1. To a clean reaction vessel add ethanol (6 ml), benzaldehyde (2.22 g, 20 mmol), ethyl acetoacetate (2.60 g, 20 mmol), urea (1.44 g, 20 mmol), and hydrochloric acid ( $0.023 \text{ g}, 6.5 \cdot 10^{-4}$ ).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture with 20% power of the reactor for 30 min. to reflux ethanol during the irradiation.
5. Allow the reaction mixture to cool to room temperature, concentrate the solution by rotary evaporation and recrystallize the product from ethanol; m.p.  $200\text{-}202^\circ\text{C}$ , yield  $> 80\%$ .

**7.1.3. Biphenyl**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

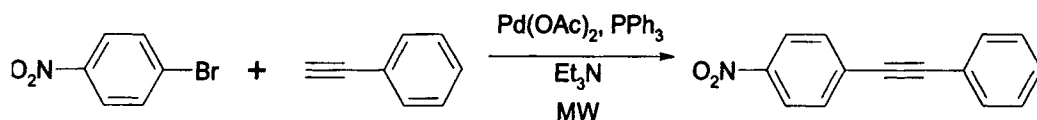
Iodobenzene	0.20 g, 1.0 mmol	harmful by inhalation, ingestion, by skin contact, may cause blisters, may be carcinogenic
Phenyl boronic acid	0.12 g, 1.0 mmol	may be fatal if inhaled, harmful if absorbed through skin, material is extremely destructive to the tissue of the eyes and skin
Palladium acetate (II)	62 mg, 0.28 mmol	avoid contact with skin and eyes
Potassium fluoride	38 mg, 0.67 mmol	harmful by inhalation, ingestion and through skin contact, very destructive of mucous membranes
Poly(ethylene glycol)	2.0 g	may be harmful by inhalation, ingestion or through skin contact, may act as an irritant

**Method [59]**

1. To a clean reaction vessel add poly(ethylene glycol) (2 g), iodobenzene (0.20 g, 1.0 mmol), phenyl boronic acid (0.12 g, 1.0 mmol), palladium acetate (II) (62 mg, 0.28 mmol), and potassium fluoride (38 mg, 0.67 mmol ).
2. Stirr the mixture for 10-20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 30% power of the reactor for 10 min. to reach the final temperature 190°C .
5. Allow the reaction mixture to cool to room temperature, extract the product into diethyl ether (2 x 10 ml), and let the solvent to evaporate.
6. Recrystallize the solid from ethanol to afford biphenyl; m.p. 68-70°C , yield: 75%.

## 7.1.4. 1-Nitro-4-phenylethynyl-benzene

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

Phenylacetylene	1.53 g, 15 mmol	flammable, lachrymator, irritant
p-Bromonitrobenzene	2.02 g, 10 mmol	toxic if swallowed or inhaled, may lead to cyanosis, danger of cumulative effects
Triethylamine	10 ml, 70 mmol	extremely flammable, harmful by ingestion, inhalation and if absorbed through the skin, chronic exposure may cause liver damage, lachrymator
Triphenylphosphine	6.0 mg, 0.019 mmol	harmful if swallowed or inhaled. causes irritation to skin, eyes and respiratory tract
Palladium acetate (II)	2.0 mg, $8.9 \cdot 10^{-3}$ mmol	avoid contact with skin and eyes

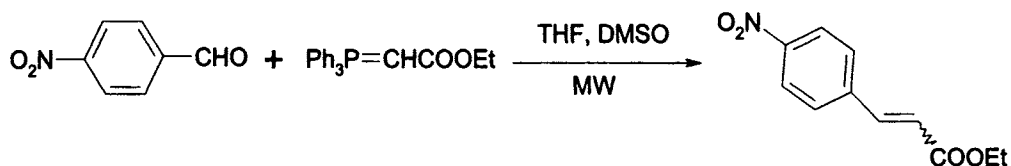
**Method [60]**

1. To a clean reaction vessel add triethylamine (10 ml, 70 mmol), phenylacetylene (1.53 g, 15 mmol), p-promonitrobenzene (2.02 g, 10 mmol), triphenylphosphine (6.0 mg, 0.019 mmol), and palladium acetate (II) (2.0 mg,  $8.9 \cdot 10^{-3}$  mmol).
2. Stir the mixture for 10-20 s with a spatula at room temperature to ensure efficient mixing.

3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 10 min. to reach the final temperature 100°C .
5. Allow the reaction mixture to cool to room temperature, and add 2M hydrochloric acid (42 ml). Collect the insoluble product by filtration and purified by sublimation at 115°C at 2-3 mmHg.
6. Recrystallize the solid from 70% ethanol/water mixture and leave it in fridge overnight to complete crystallization.

### 7.1.5. 3-(4-Nitro-phenyl)-acrylic acid ethyl ester

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

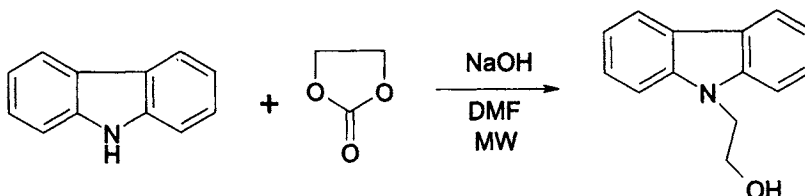
p-Nitrobenzaldehyde	0.76 g, 5 mmol	harmful by inhalation, in contact with skin and if swallowed
Carbethoxymethylene triphenylphosphorane	1.76 g, 5 mmol	avoid contact with skin and eyes
THF	8.5 ml	may generate explosive peroxides in storage if in contact with air, highly flammable, may be harmful by inhalation, ingestion or skin absorption, long-term exposure may lead to kidney or liver damage, irritant, may cause narcotic effects
DMSO	0.5 ml	skin, eye and respiratory system irritant

**Method [61]**

1. To a clean reaction vessel add THF(8.5 ml), DMSO (0.5 ml), p-pitrobenzaldehyde (0.76 g, 5 mmol), and carbethoxymethylene triphenylphosphorane (1.76 g, 5 mmol).
2. Stir the mixture for 10 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 30% power of the reactor for 10 min. to reach the final temperature 70°C .
5. Allow the reaction mixture to cool to room temperature, concentrate the solution by rotary evaporation and recrystallize the product from ethanol; m.p. 137-139°C , yield > 60%.

## 7.1.6. 2-Carbazol-9-yl-ethanol

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)

Reaction vessel (150 ml round-bottomed flask)

Long-neck adapter (Figure 4.1)

Reflux condenser

**Materials**

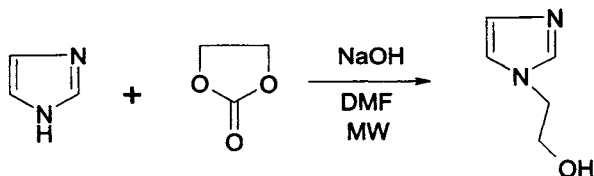
Carbazole	5.0 g, 29 mmol	harmful by inhalation or ingestion, may be harmful in contact with skin, suspected carcinogen
Ethylene carbonate	11.5 g, 131 mmol	irritant, risks of serious damage to eyes
DMF	26 ml	harmful by inhalation, ingestion or skin contact, may act as a carcinogen, ingestion or absorption through skin may be fatal, exposure may result in foetal death, Long-term exposure may result in kidney or liver damage, irritant
Sodium hydroxide	1.0 g, 25 mmol	very corrosive, causes severe burns, may cause serious permanent eye damage, very harmful by ingestion, harmful by skin contact or by inhalation of dust

**Method [62]**

1. To a round-bottomed flask (150 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add carbazole (5.0 g, 29 mmol), ethylene carbonate (11.5 g, 131 mmol), DMF (26 ml) and powdered sodium hydroxide (1.0 g, 25 mmol).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture to 145-150°C for 45 min. whilst stirring.
4. Remove carefully the hot flask from the microwave reactor and pour into a large amount of cold water with ice.
5. Filter the precipitated solid, and recrystallize the product from ethanol; m.p. 78-80°C, yield > 65%.

**7.1.7. 2-Imidazol-1-yl-ethanol**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)

Reaction vessel (150 ml round-bottomed flask)

Long-neck adapter (Figure 4.1)

Reflux condenser



**Materials**

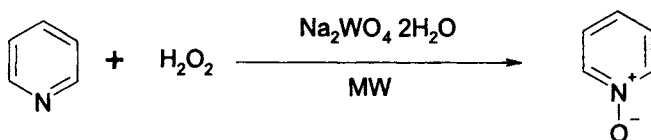
Imidazole	5.5 g, 81 mmol	corrosive - causes burns, harmful by ingestion or inhalation, may cause serious burns to the skin or eyes
Ethylene carbonate	11.5 g, 74 mmol	irritant, risks of serious damage to eyes
DMF	25 ml	harmful by inhalation, ingestion or skin contact, may act as a carcinogen, ingestion or absorption through skin may be fatal, exposure may result in foetal death, Long-term exposure may result in kidney or liver damage, irritant
Sodium hydroxide	0.80 g, 25 mmol	very corrosive, causes severe burns, may cause serious permanent eye damage, very harmful by ingestion, harmful by skin contact or by inhalation of dust

**Method [62]**

1. To a round-bottomed flask (250 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add imidazole (5.5 g, 81 mmol), ethylene carbonate (11.5 g, 131 mmol), DMF (26 ml), and powdered sodium hydroxide (1.0 g, 25 mmol).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture to 145-150°C for 45 min. whilst stirring.
4. Allow the reaction mixture to cool to room temperature and pour carefully into a large amount of cold water with ice. THEN extract the mixture with ethyl acetate in a separating funnel.
5. Concentrate the solution by rotary evaporation to obtain the product as an oil, yield > 50%.

### 7.1.8. Pyridine N-oxide

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
Reaction vessel (50 ml round-bottomed flask)  
Long-neck adapter (Figure 4.1)  
Reflux condenser

#### Materials

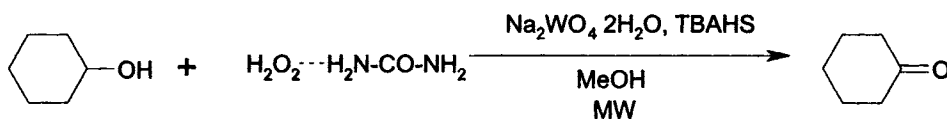
Pyridine	1.6 g, 20 mmol	flammable, harmful by ingestion, inhalation and if absorbed through skin, may affect fertility, severe eye and skin irritant - may cause burns, long-term exposure may cause liver, kidney or CNS damage
Hydrogen peroxide (30% solution)	10.2 g, 90 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
Sodium tungstate dihydrate	0.10 g, 0.30 mmol	may act as an irritant

**Method [63]**

1. To a round-bottomed flask (50 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add pyridine (1.6 g, 20 mmol), hydrogen peroxide (10.2 g, 90 mmol), and sodium tungstate dihydrate (0.10 g, 0.30 mmol).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture to 100°C for 30 min. whilst stirring.
4. Allow the reaction mixture to cool to room temperature, then extract the mixture with chloroform in a separating funnel, dry with magnesium sulfate and filter under gravity.
5. Concentrate the solution by rotary evaporation to obtain the product as an oil, yield > 60%.

**7.1.9. Cyclohexanon**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)

Reaction vessel (50 ml round-bottomed flask)

Long-neck adapter (Figure 4.1)

Reflux condenser

**Materials**

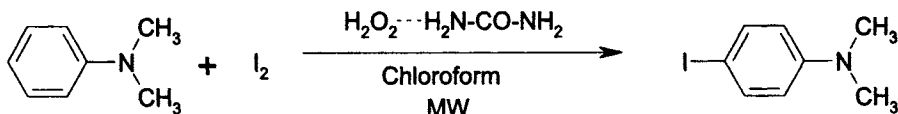
Cyclohexanol	0.61 g, 6.1 mmol	harmful by inhalation, ingestion or skin absorption, severe skin and eye irritant
Urea hydrogen peroxide (UHP)	1.35 g, 18.7 mmol	unstable, severe explosion hazard on exposure to shock or heat (!), skin, eye and respiratory irritant, corrosive - causes burns
Sodium tungstate dihydrate	0.20 g, 0.6 mmol	may act as an irritant
Tetrabutylammonium hydrogen sulfate (TBAHS)	0.20 g, 0.59 mmol	harmful, harmful if swallowed
Methanol	10 ml	highly flammable, toxic by inhalation, ingestion or skin absorption, may be a reproductive hazard, ingestion may be fatal, risk of very serious, irreversible damage if swallowed, exposure may cause eye, kidney, heart and liver damage, chronic or substantial acute exposure may cause serious eye damage, including blindness, irritant, narcotic

**Method [64]**

1. To a round-bottomed flask (50 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add methanol (10 ml), cyclohexanol (0.61 g, 6.1 mmol), sodium tungstate dihydrate (0.20 g, 0.6 mmol), and tetrabutylammonium hydrogen sulfate (TBAHS) (0.20g, 0.59 mmol).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture to 60°C and add slowly urea-hydrogen peroxide(UHP) (1.35 g, 18.7 mmol) through the reflux condenser whilst stirring; continue irradiation and stirring for a further 60 min. at reflux
4. Allow the reaction mixture to cool to room temperature, then extract the mixture with diethyl ether in a separating funnel, dry with magnesium sulfate and filter under gravity.
5. Concentrate the solution by rotary evaporation and purify the product by Kugelrohr distillation; yield > 60%.

## 7.1.10. 4-Iodo-N,N-dimethylaniline

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)

Reaction vessel (150 ml round-bottomed flask)

Long-neck adapter (Figure 4.1)

Reflux condenser

**Materials**

N,N-Dimethylaniline	3.63 g, 30 mmol	highly toxic, may be fatal if inhaled, swallowed or if absorbed through the skin, may cause serious eye damage, may act as a carcinogen, danger of cumulative effects, skin and respiratory irritant
Urea hydrogen peroxide (UHP)	1.53 g, 16.5 mmol	unstable, severe explosion hazard on exposure to shock or heat (!), skin, eye and respiratory irritant, corrosive - causes burns
Iodine	3.81 g, 15 mmol	toxic - may be fatal if swallowed or inhaled, corrosive, causes burns, harmful by inhalation and through skin absorption
Sodium sulfite	5.0 g	harmful if swallowed, may cause allergic reaction and breathing difficulties, may cause irritation to skin, eyes, and respiratory tract

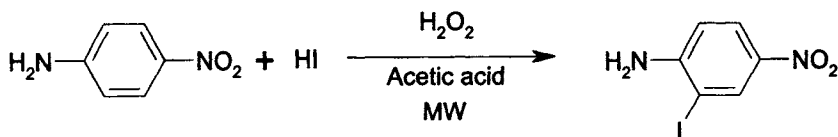
Chloroform	50 ml	causes cancer in laboratory animals, and is listed as a probable human carcinogen, inhalation and ingestion are harmful and may be fatal, may cause reproductive damage, prolonged or repeated skin contact may cause dermatitis
Water	50 ml	non-hazardous

**Method [65]**

1. To a round-bottomed flask (150 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add urea-hydrogen peroxide (UHP) (1.53 g, 16.5 mmol), finely powdered diiodine (3.81 g 156 mmol) suspended in chloroform (50 ml), and N,N-dimethylaniline (3.63 g, 30 mmol).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture whilst stirring to ensure a slight, uninterrupted reflux of the solvent for 10 min.
4. Allow the reaction mixture to cool to room temperature, then pour into vigorously stirred aqueous solution of sodium sulfite (5 g in 50 ml of water).
5. Separate the organic layer in a separating funnel, dry with magnesium sulfate and filter under gravity.
6. Concentrate the solution by rotary evaporation and recrystallize the product from ethanol, m.p. 80-81, yield > 70%.

**7.1.11. 2-Iodo-4-nitroaniline**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)

Reaction vessel (150 ml round-bottomed flask)

Long-neck adapter (Figure 4.1)

Reflux condenser

**Materials**

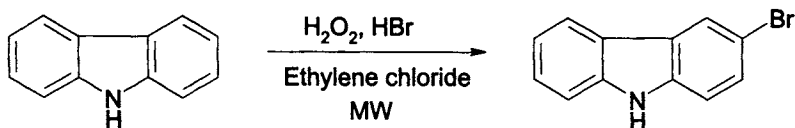
p-Nitroaniline	0.41 g, 3.0 mmol	may decompose explosively in the presence of initiators, highly toxic by inhalation, ingestion and if absorbed through skin, may cause cumulative effects
Hydroiodic acid (58% solution)	0.72 g, 3.3 mmol	may cause congenital malformation in the foetus, corrosive - causes burns, harmful if swallowed, inhaled or in contact with skin
Hydrogen peroxide (30% solution)	0.37 g, 3.3 mmol	corrosive, causes burns, after contact with skin wash immediately with plenty of water
Acetic acid (80%)	25 ml	strongly corrosive and causes serious burns, very harmful if swallowed, lachrymator

**Method [66]**

1. To a round-bottomed flask (150 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add acetic acid (25 ml, 80% solution), p-nitroaniline (0.41 g, 3.0 mmol), and hydroiodic acid (0.42 g, 3.3 mmol, 58% solution).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture to 100°C whilst stirring and slowly add (dropwise) hydrogen peroxide (0.37 g, 3.3 mmol, 30% solution) through the reflux condenser; continue irradiation and stirring for a further 30 min.
4. Allow the reaction mixture to cool to room temperature, then pour into a large amount of cool water, and filter off the solid product .
5. Recrystallize the solid from ethanol; m.p. 105-7°C , yield: 50%.

## 7.1.12. 3-Bromocarbazole

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
 Reaction vessel (150 ml round-bottomed flask)  
 Long-neck adapter (Figure 4.1)  
 Reflux condenser

**Materials**

Carbazole	0.51 g, 3.0 mmol	harmful by inhalation or ingestion, may be harmful in contact with skin, suspected carcinogen
Hydrogen peroxide (30% solution)	0.37 g, 3.3 mmol	corrosive, causes burns, after contact with skin wash immediately with plenty of water
Hydrobromic acid (40% solution)	0.66 g, 3.3 mmol	causes severe burns, toxic if swallowed, harmful in contact with skin, and through ingestion or inhalation, respiratory irritant
Ethylene chloride	30 ml	highly flammable, probable human carcinogen, causes liver damage, mutagen, toxic, may cause systemic effects, narcotic

**Method [66]**

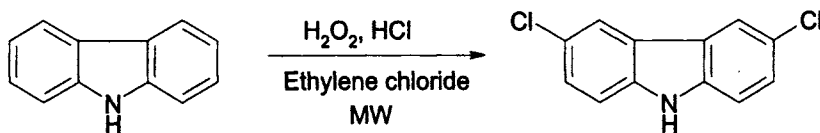
1. To a round-bottomed flask (150 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add ethylene chloride (25 ml), carbazole (0.51 g, 3.0 mmol), and hydrobromic acid (40% solution) (0.66 g, 3.3 mmol).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).



3. Irradiate the reaction mixture to 50°C whilst stirring and slowly add (dropwise) hydrogen peroxide (0.37 g, 3.3 mmol, 30% solution) in a ethylene chloride solution (5 ml) through the reflux condenser; continue irradiation and stirring for a further 25 min.
4. Allow the reaction mixture to cool to room temperature and separate the organic layer in a separating funnel, dry with magnesium sulfate and filter under gravity.
5. Concentrate the solution by rotary evaporation and recrystallize the product from n-heptane; m.p. 197-199°C, yield > 70%.

### 7.1.13. 3,6-Dichlorocarbazole

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
Reaction vessel (150 ml round-bottomed flask)  
Long-neck adapter (Figure 4.1)  
Reflux condenser

#### Materials

Carbazole                      0.51 g, 3.0 mmol

Hydrogen peroxide      2.3 g, 20 mmol  
(30% solution)

Sodium tungstate      0.10 g, 0.30 mmol  
dihydrate

harmful by inhalation or  
ingestion, may be harmful in  
contact with skin, suspected  
carcinogen  
corrosive, causes burns, after  
contact with skin wash  
immediately with plenty of water  
may act as an irritant

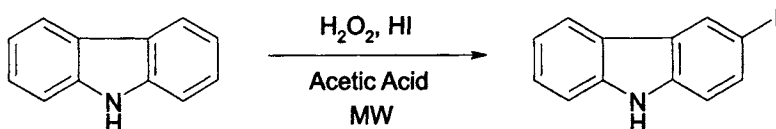
Hydrochloric acid (36 %)	2.2 g, 20 mmol	extremely corrosive, inhalation of vapour can cause serious injury, ingestion may be fatal, liquid can cause severe damage to skin and eyes
Ethylene chloride	30 ml	highly flammable, probable human carcinogen, causes liver damage, mutagen, toxic, may cause systemic effects, narcotic

### Method [66]

1. To a round-bottomed flask (150 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add ethylene chloride (25 ml), carbazole (0.51 g, 3.0 mmol), and hydrochloric acid (2.2 g, 20 mmol, 36 % solution).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture to 75°C whilst stirring and slowly add (dropwise) hydrogen peroxide (2.3 g, 20 mmol, 30% solution) in a ethylene chloride solution (5 ml) through the reflux condenser; continue irradiation and stirring for a further 25 min.
4. Allow the reaction mixture to cool to room temperature and separate the organic layer in a separating funnel, dry with magnesium sulfate and filter under gravity.
5. Concentrate the solution by rotary evaporation and recrystallize the product from n-heptane; m.p. 203-205°C, yield > 60%.

#### 7.1.14. 3-Iodocarbazole

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



### Equipment

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
Reaction vessel (150 ml round-bottomed flask)  
Long-neck adapter (Figure 4.1)  
Reflux condenser

**Materials**

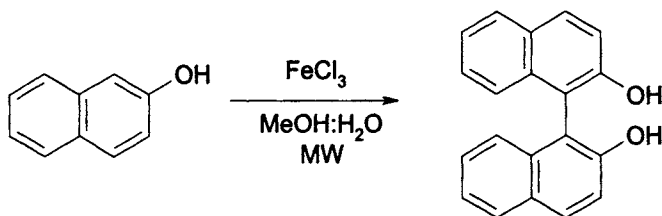
Carbazole	0.51 g, 3.0 mmol	harmful by inhalation or ingestion, may be harmful in contact with skin, suspected carcinogen
Hydroiodic acid	0.73 g, 3.3 mmol	may cause congenital malformation in the foetus, corrosive - causes burns, harmful if swallowed, inhaled or in contact with skin
Hydrogen peroxide (30% solution)	0.37 g, 3.3 mmol	corrosive, causes burns, after contact with skin wash immediately with plenty of water
Acetic acid	30 ml	strongly corrosive and causes serious burns, very harmful if swallowed, lachrymator

**Method [66]**

1. To a round-bottomed flask (150 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add acetic acid (25 ml), carbazole (0.51 g, 3.0 mmol), and hydroiodic acid (0.73 g, 3.3 mmol).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture to 100°C whilst stirring and slowly add (dropwise) hydrogen peroxide (0.37 g, 3.3 mmol, 30% solution) in a ethylene chloride solution (5 ml) through the reflux condenser; continue irradiation and stirring for a further 25 min.
4. Allow the reaction mixture to cool to room temperature and pour carefully into a large amount of cold water with ice.
5. Filter the precipitated solid, and recrystallize the product from ethanol or n-heptane; m.p. 192-4°C, yield > 70%.

## 7.1.15. 1,1'-Bi-2-naphthol

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)

Reaction vessel (250 ml round-bottomed flask)

Long-neck adapter (Figure 4.1)

Reflux condenser

**Materials**

2-Naphthol                      1.4 g, 5.0 mmol

harmful if swallowed or inhaled,  
may be harmful in contact with  
the skin, eye, skin and respiratory  
irritant

Iron (III) chloride    2.7 g, 10 mmol  
hexahydrate

corrosive - causes burns, harmful  
by inhalation, ingestion and  
through skin contact, respiratory,  
eye and skin irritant

Methanol                      50 ml

highly flammable, toxic by  
inhalation, ingestion or skin  
absorption, may be a reproductive  
hazard, ingestion may be fatal,  
risk of very serious, irreversible  
damage if swallowed, exposure  
may cause eye, kidney, heart and  
liver damage, chronic or  
substantial acute exposure may  
cause serious eye damage,  
including blindness, irritant,  
narcotic

Water                      50 ml

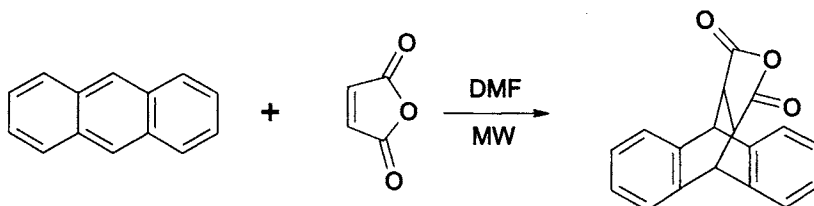
non-hazardous

**Method [67]**

1. To a round-bottomed flask (250 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add water (50 ml), methanol (50 ml), naphthol (1.4 g, 5.0 mmol), and iron (III) chloride hexahydrate (2.7 g, 10 mmol).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture for 1 h in the temperature range of 65-80°C whilst stirring.
4. Allow the reaction mixture to cool to room temperature
5. Filter the precipitated solid at the pump through a Buchner funnel, wash with the mixture methanol/water (50%/50%) and dry below 60°C (m.p. 214-217°C ). Yields > 60% are typical.

**7.1.16. 9,10-Dihydroanthraceno-9,10- $\alpha,\beta$ -succinic anhydride**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2a)

Adapter (Figure 4.2f)

Cold finger

**Materials**

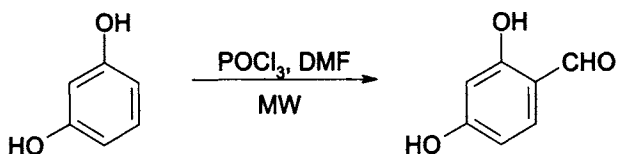
Anthracene	1.32 g, 7.4 mmol	harmful by inhalation or ingestion, may be harmful in contact with skin, suspected carcinogen
Maleic anhydride	0.73 g, 7.4 mmol	harmful if swallowed, inhaled or absorbed through the skin, corrosive - causes burns, irritant
DMF	10 ml	harmful by inhalation, ingestion or skin contact, may act as a carcinogen, ingestion or absorption through skin may be fatal, exposure may result in foetal death, Long-term exposure may result in kidney or liver damage, irritant

**Method**

1. To a clean reaction vessel add DMF (10 ml), anthracene (1.32 g, 7.4 mmol) and maleic anhydride (0.73 g, 7.4 mmol).
2. Stir the mixture for 10 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture to 150-150°C whilst stirring for 25 min.
5. Allow the reaction mixture to cool to room temperature and pour into a large amount of vigorously stirred cold water with ice.
6. Collect the product by filtration, wash twice with a small amount of water, and let dry at least one day before taking the melting point; m.p. 258-262°C, yield > 70%.

## 7.1.17. 2,4-Dihydroxybenzaldehyde

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)

Reaction vessel (150 ml round-bottomed flask)

Long-neck adapter (Figure 4.1)

Reflux condenser

**Materials**

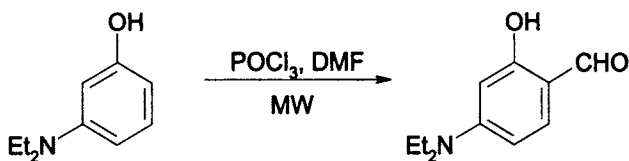
1,3-Dihydroxybenzene (resorcinol)	4.13 g, 37 mmol	harmful if swallowed or inhaled and in contact with skin, Skin and respiratory irritant, eye contact may lead to serious damage
Phosphorus oxychloride	7.0 ml, 7.5 mmol	reacts violently with water, may be fatal if inhaled, swallowed or absorbed through the skin, may cause serious and permanent eye damage, including blindness, causes burns, If inhaled may cause delayed lung injury
DMF	20 ml	harmful by inhalation, ingestion or skin contact, may act as a carcinogen, ingestion or absorption through skin may be fatal, exposure may result in foetal death, long-term exposure may result in kidney or liver damage, irritant

## Method

1. To a round-bottomed flask (100 ml) equipped with a magnetic stirrer bar, add DMF (20 ml) and then slowly phosphorous oxychloride (7.0 ml, 75 mmol).
2. Stir the solution at room temperature for 1 h and then add portion-wise 1,3-dihydroxybenzene (resorcinol) (4.13 g, 37 mmol) to the stirred solution.
3. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
4. Irradiate the reaction mixture at 65°C whilst stirring for 1 h.
5. Remove carefully the hot flask from the microwave reactor and pour into a large amount of vigorously stirred cold water with ice.
6. Extract the product into ethyl acetate (2 x 75 ml) in a separating funnel, dry with magnesium sulfate and filter under gravity.
7. Concentrate the solution by rotary evaporation and recrystallize the product from ethanol; m.p. 135-137°C, yield > 80%.

### 7.1.18. 4-Diethylaminosalicylaldehyde

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



## Equipment

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
Reaction vessel (150 ml round-bottomed flask)  
Long-neck adapter (Figure 4.1)  
Reflux condenser



## Materials

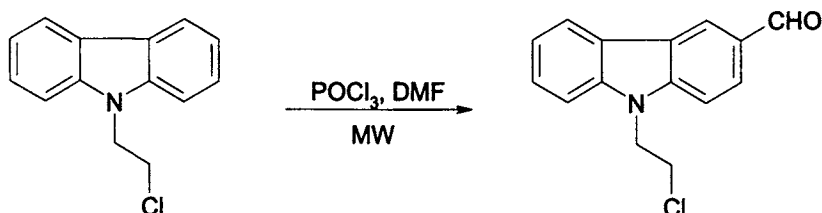
3-Diethylaminophenol	6.2 g, 37 mmol	toxic, toxic if swallowed
Phosphorus oxychloride	7.0 ml, 7.5 mmol	reacts violently with water, may be fatal if inhaled, swallowed or absorbed through the skin, may cause serious and permanent eye damage, including blindness, causes burns, If inhaled may cause delayed lung injury
DMF	20 ml	harmful by inhalation, ingestion or skin contact, may act as a carcinogen, ingestion or absorption through skin may be fatal, exposure may result in foetal death, Long-term exposure may result in kidney or liver damage, irritant

## Method

1. To a round-bottomed flask (100 ml) equipped with a magnetic stirrer bar, add DMF (20 ml) and then slowly phosphorous oxychloride (7.0 ml, 75 mmol).
2. Stir the solution at room temperature for 1 h and then add portion-wise 3-diethylaminophenol (6.2 g, 37 mmol) to the stirred solution.
3. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
4. Irradiate the reaction mixture at 65°C whilst stirring for 1 h.
5. Remove carefully the hot flask from the microwave reactor and pour into a large amount of vigorously stirred cold water with ice.
6. Extract the product into ethyl acetate (2 x 75 ml) in a separating funnel, dry with magnesium sulfate and filter under gravity.
7. Concentrate the solution by rotary evaporation and recrystallize the product from ethanol; m.p. 60-62°C , yield > 80%.

## 7.1.19. 9-(2-Chloroethyl)carbazole-3-carbaldehyde

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
 Reaction vessel (100 ml round-bottomed flask)  
 Long-neck adapter (Figure 4.1)  
 Reflux condenser

**Materials**

9-(2-Chloroethyl)-carbazole	4.6 g, 20 mmol	none data available
Phosphorus oxychloride	7.0 ml, 7.4 mmol	reacts violently with water, may be fatal if inhaled, swallowed or absorbed through the skin, may cause serious and permanent eye damage, including blindness, causes burns, If inhaled may cause delayed lung injury
DMF	20 ml	harmful by inhalation, ingestion or skin contact, may act as a carcinogen, ingestion or absorption through skin may be fatal, exposure may result in foetal death, Long-term exposure may result in kidney or liver damage, irritant

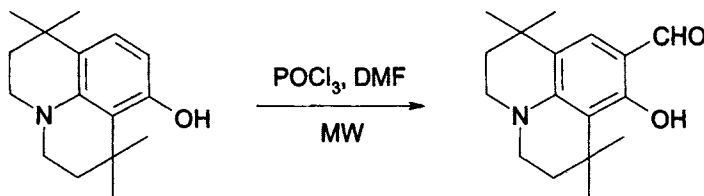
**Method**

1. To a round-bottomed flask (100 ml) equipped with a magnetic stirrer bar, add DMF (20 ml) and then slowly phosphorous oxychloride (7.0 ml, 75 mmol).

2. Stir the solution at room temperature for 1 h and then add portion-wise 9-(2-chloroethyl)carbazole (4.6 g, 20 mmol) to the stirred solution.
3. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
4. Irradiate the reaction mixture at 100°C whilst stirring for 1 h.
5. Remove carefully the hot flask from the microwave reactor and pour into a large amount of vigorously stirred cold water with ice.
6. Filter the precipitated solid, and recrystallize the product from ethanol; m.p. 166-168°C, yield > 75%.

#### 7.1.20. 8-Hydroxy-1,1,7,7-tetramethyljulolidine -9-carboxaldehyde

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
Reaction vessel (50 ml round-bottomed flask)  
Long-neck adapter (Figure 4.1)  
Reflux condenser

**Materials**

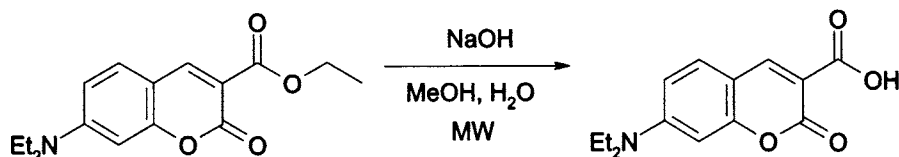
8-Hydroxy-1,1,7,7-tetramethyljulolidine	2.9 g, 12 mmol	avoid contact with skin and eyes
Phosphorus oxychloride	1.75 ml, 19 mmol	reacts violently with water, may be fatal if inhaled, swallowed or absorbed through the skin, may cause serious and permanent eye damage, including blindness, causes burns, if inhaled may cause delayed lung injury
DMF	10 ml	harmful by inhalation, ingestion or skin contact, may act as a carcinogen, ingestion or absorption through skin may be fatal, exposure may result in foetal death, long-term exposure may result in kidney or liver damage, irritant

**Method [68]**

1. To a round-bottomed flask (50 ml) equipped with a magnetic stirrer bar, add DMF (10 ml) and then slowly phosphorous oxychloride ( 1.75 ml, 19 mmol).
2. Stir the solution at room temperature for 1 h and then add portion-wise 8-hydroxy-1,1,7,7-tetramethyljulolidine (2.9 g, 12 mmol) to the stirred solution.
3. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
4. Irradiate the reaction mixture at 65°C whilst stirring for 1 h.
5. Remove carefully the hot flask from the microwave reactor and pour into a large amount of vigorously stirred cold water.
6. Extract the product into the mixture of n-hexane/ethyl acetate (1:1) (2 x 40 ml) in a separating funnel, dry with magnesium sulfate and filter under gravity.
7. Concentrate the solution by rotary evaporation, pure by flash chromatography (n-hexane/ethyl acetate 6:1, silica gel).
8. Remove again the solvents by rotary evaporation and recrystallize the product from a hexane/ethyl acetate mixture; m.p. 74-76°C , yield > 70%.

## 7.1.21. 7-Diethylamino-2-oxo-2H-chromene-3-carboxylic acid

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
 Reaction vessel (150 ml round-bottomed flask)  
 Long-neck adapter (Figure 4.1)  
 Reflux condenser

**Materials**

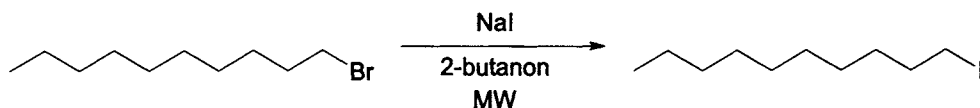
Ethyl 7-diethylamino-2-oxo-2H-chromene-3-carboxylate	2.9 g, 10 mmol	none date available
Sodium hydroxide	2.50 g, 62 mmol	very corrosive, causes severe burns, may cause serious permanent eye damage, very harmful by ingestion, harmful by skin contact or by inhalation of dust
Methanol	25 ml	highly flammable, toxic by inhalation, ingestion or skin absorption, may be a reproductive hazard, ingestion may be fatal, risk of very serious, irreversible damage if swallowed, exposure may cause eye, kidney, heart and liver damage, chronic or substantial acute exposure may cause serious eye damage, including blindness, irritant, narcotic
Water	25 ml	non-hazardous

**Method [62]**

1. To a round-bottomed flask (150 ml) equipped with a magnetic stirrer bar, add methanol (25 ml), water (25 ml), sodium hydroxide (2.5 g, 62 mmol), and ethyl 7-diethylamino-2-oxo-2H-chromene-3-carboxylate (2.9 g, 10 mmol).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture at 65°C whilst stirring for 1 h.
4. Allow the reaction mixture to cool to room temperature, and a diluted hydrochloric acid (5% aq. solution) to neutralize the solution and precipitate the crude product.
5. Filter off the crude product and recrystallize from ethanol; m.p. 186-189°C , yield > 50%.

**7.1.22. 1-Iododecane**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

1-Bromodecane	1.06 g, 10 mmol	may be harmful or act as an irritant - toxicology not fully investigated
Sodium iodate	1.49 g, 10 mmol	harmful if swallowed or inhaled, may cause sensitization
2-Butanone	6 ml	highly flammable, severe eye irritant, can cause CNS depression, skin irritant, may be harmful by ingestion, inhalation or through skin contact, may cause dermatitis

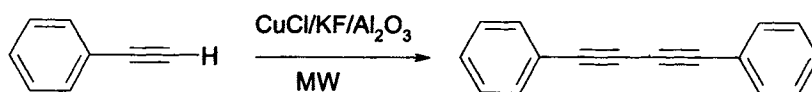
**Method [50]**

1. To a clean reaction vessel add 1-bromodecane (1.1 g, 10 mmol), sodium iodate (1.5 g, 10 mmol), and 2-butanone (6 ml).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 10 min. to reach temperature ca. 80-85°C during the irradiation.
5. Allow the reaction mixture to cool to room temperature and purify the crude product by Kugelrohr distillation; b.p. 130-132°C /15 mmHg, yield > 60%.

## 7.2. Reactions of reagents supported on mineral supports

### 7.2.1. Diphenylbutadiyne

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

### Materials

Phenylacetylene	0.10 g, 10 mmol	<b>flammable, lachrymator, irritant moisture sensitive, harmful if swallowed, irritant</b>
Cupric chloride (I)	0.500 g, 3.7 mmol	
Potassium fluoride/ Aluminium oxide	0.60 g, 10 mmol	<b>harmful by inhalation or ingestion, irritate eyes or skin harmful by inhalation, ingestion or skin contact, may act as a carcinogen, ingestion or absorption through skin may be fatal, exposure may result in foetal death, Long-term exposure may result in kidney or liver damage, irritant</b>
DMF		

### Method [69]

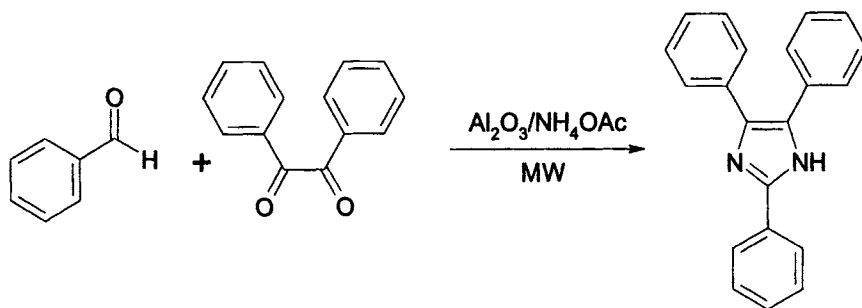
1. To a clean, dry reaction vessel add potassium fluoride adsorbed on alumina oxide (40 wt.%, Aldrich) (0.60 g), cupric chloride (I) (0.50 g, 3.7 mmol), phenylacetylene (0.10 g, 1.0 mmol), and a few drops of DMF.
2. Stirr the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).



4. Rotating the reaction vessel (if possible), heat the mixture with 30% power of the reactor for 50 min. to reach the final temperature ca. 150°C .
5. Allow the reaction mixture to cool to room temperature, add hexane (10 ml) and stir for the mixture for 20 s.
6. Filter the mixture and purify the product by column chromatography (silica gel); m.p. 85-87°C , yield > 60%.

### 7.2.2. 2,4,5-Triphenylimidazole

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

#### Materials

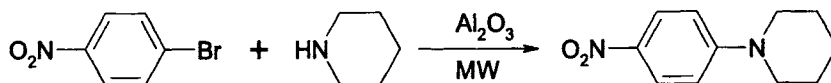
1,2-Diphenylethanedione	0.10 g, 0.50 mmol	skin, eye and respiratory irritant, may be harmful
Benzaldehyde	0.053 g, 0.50 mmol	eye irritant, harmful by inhalation or ingestion, may be harmful by skin contact and cause allergic reaction
Aluminium oxide	9.3 g	harmful by inhalation or ingestion, irritate eyes or skin
Ammonium acetate	4.4 g, 57 mmol	may be harmful by inhalation or ingestion, irritant

**Method [70]**

1. To a clean reaction vessel add aluminium oxide (9.3 g), ammonium acetate (4.4 g, 57 mmol), 1,2-diphenylethanedione (0.10 g, 0.50 mmol), and benzaldehyde (0.053 g, 0.50 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture with 20% power of the reactor for 10 min. to reach the final temperature ca. 120°C .
5. Allow the reaction mixture to cool to room temperature, and wash with the mixture of acetone/triethylamine (7:3, 3 x 10 ml) to extract the product.
6. Dry the extract with magnesium sulfate filter under gravity, and concentrate the solution by rotary evaporation.
7. Purify the product by column chromatography (hexane/ethyl acetate 4:1, silica gel); m.p. 275-277°C , yield > 60%.

**7.2.3. 1-(4-Nitro-phenyl)-piperidine**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

### Materials

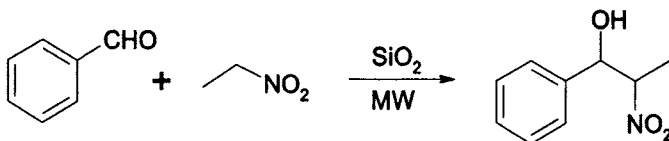
p-Bromonitrobenzene	2.02 g, 10 mmol	toxic if swallowed or inhaled, may lead to cyanosis, danger of cumulative effects
Piperidine	1.02 g, 12 mmol	poison, may be fatal if inhaled or swallowed, severe irritant, contact with the eyes may lead to permanent damage
Aluminium oxide	5.0 g, 50 mmol	harmful by inhalation or ingestion, irritate eyes or skin

### Method [71]

1. To a clean reaction vessel add aluminium oxide (5.0 g), piperidine (1.0 g, 12 mmol), and p-bromonitrobenzene (2.0 g, 10 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 10 min. to reach temperature ca. 180°C, cool to 100°C and then heat for another 10 min. to reach the final temperature ca. 160°C.
5. Allow the reaction mixture to cool to room temperature, and charge directly on the top chromatography column (silica gel).
6. Purify the product by column chromatography (hexane/ethyl acetate 7:3); m.p. 102-104°C, yield > 60%.

#### 7.2.4. 2-Nitro-1-phenyl-propan-1-ol

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

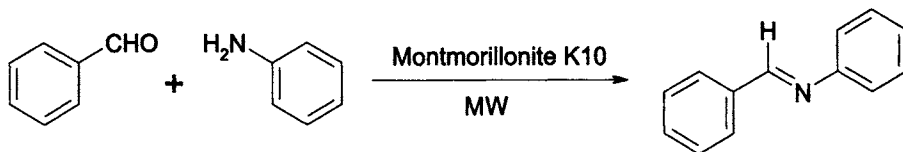
Benzaldehyde	1.06 g, 10 mmol	eye irritant, harmful by inhalation or ingestion, may be harmful by skin contact and cause allergic reaction
Nitroethane	0.75 g, 10 mmol	harmful if swallowed, inhaled or absorbed through skin, irritant, may cause cyanosis
Silica gel	5.0 g	harmful if inhaled, irritant, chronic exposure to the dust may be very harmful

**Method [72]**

1. To a clean reaction vessel add silica gel (5.0 g), benzaldehyde (1.0 g, 10 mmol), and nitroethane (0.75 g, 10 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 50% power of the reactor for 20 min. to reach the final temperature ca. 150°C .
5. Allow the reaction mixture to cool to room temperature, and extract the product into dichloromethane (2 x 15 ml) on a filtering funnel.
6. Remove the solvent by rotary evaporation and purify the product by column chromatography (silica gel); yield > 60%.

### 7.2.5. Phenyl-[1-phenyl-methylidene]amine

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

#### Materials

Benzaldehyde	0.10 g, 1.0 mmol	eye irritant, harmful by inhalation or ingestion, may be harmful by skin contact and cause allergic reaction
Aniline	0.093 g, 1.0 mmol	toxic, possible carcinogen, mutagen, and sensitizer, cyanotic reagent, readily absorbed through the skin
Montmorillonite K10	20 mg	inhalation of dust may cause irritation to the respiratory tract

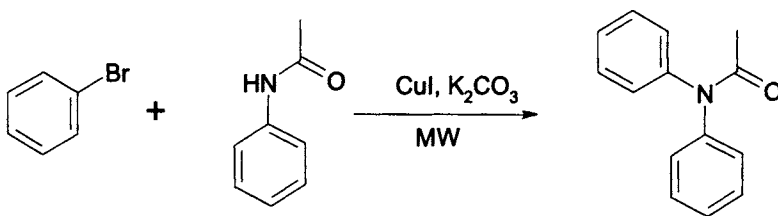
#### Method [73]

1. To a clean reaction vessel add montmorillonite K10 (0.020 g), aniline (0.092 g, 1.0 mmol), and benzaldehyde (0.10 g, 1.0 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 30% power of the reactor for 10 min. to reach the final temperature ca. 80°C .
5. Allow the reaction mixture to cool to room temperature, and extract the product into dichloromethane (2 x 15 ml) on a filtering funnel.

6. Remove the solvent by rotary evaporation and purify the product by column chromatography; m.p. 50-52°C, yield > 60%.

### 7.2.6. N,N-Diphenylacetamide

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2a)

Adapter (Figure 4.2f)

Cold finger

#### Materials

Acetanilide	3.38 g, 25 mmol	irritant, may be harmful if swallowed.
Bromobenzene	3.95 g, 38 mmol	harmful if inhaled, may be harmful if swallowed or absorbed through the skin, severe irritant
1-Methylpyrrolidone (NMP)	5 ml	skin, eye and respiratory irritant
Copper iodide (I)	0.50 g 2.5 mmol	harmful if swallowed, may be harmful if inhaled or absorbed through the skin
Potassium carbonate	3.45 g, 25 mmol	may seriously irritate respiratory system and eyes, skin irritant

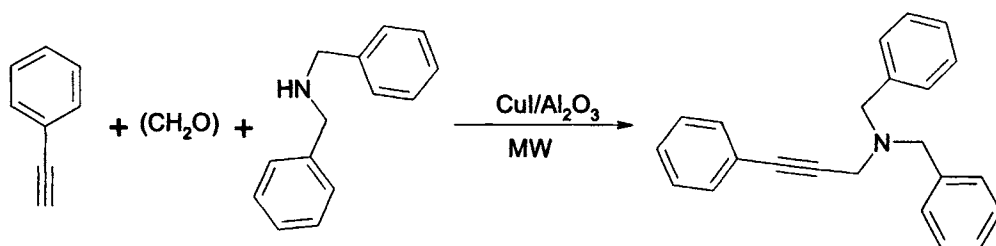
#### Method [74]

1. To a clean reaction vessel add potassium carbonate (3.4 g, 25 mmol), acetanilide (3.4 g, 25 mmol), bromobenzene (4.0 g, 38 mmol), 1-methylpyrrolidone (NMP) (5 ml), and copper iodide (I) (0.50 g 2.5 mmol).

2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 20 min. to reach the final temperature ca. 200°C .
5. Allow the reaction mixture to cool to room temperature, and extract the product into diethyl ether (200 ml) on a filtering funnel.
6. Wash the diethyl layer with ammonium hydroxide (5% aq. solution) (3 x 10 ml) and sodium bicarbonate (5% aq. solution) (3 x 10 ml).
7. Remove the solvent by rotary evaporation and purify the product by flash chromatography (petroleum ether/ethyl acetate 3:1, silica gel); m.p. 101-103°C , yield > 65%.

### 7.2.7. Dibenzyl-(3-phenyl-prop-2-ynyl)amine

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

Phenylacetylene	0.10 g, 1.0 mmol	flammable, lachrymator, irritant
Dibenzylamine	0.20 g, 1.0 mmol	harmful if swallowed, skin irritant, may be an inhalation irritant
Paraformaldehyde	0.090 g	ingestion may be fatal, may cause heritable genetic damage, may cause irreversible damage to sight, may cause skin or eye burns or irritation, can cause severe burning of mouth and stomach
Copper iodide (I)	0.57 g 3.0 mmol	harmful if swallowed, may be harmful if inhaled or absorbed through the skin
Aluminium oxide	1.0 g	harmful by inhalation or ingestion, irritate eyes or skin

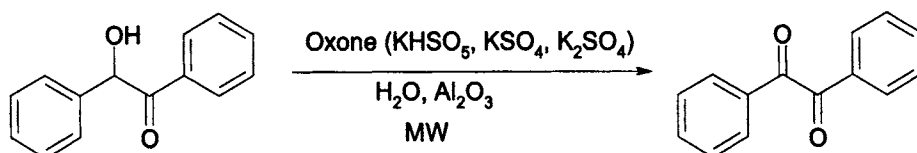
**Method [75]**

1. To a clean reaction vessel add aluminium oxide (1.0 g), phenylacetylene (0.10 g, 1.0 mmol), dibenzylamine (0.20 g, 1.0 mmol), paraformaldehyde (0.090 g), and copper iodide (I) (0.57 g 3.0 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 30% power of the reactor for 10 min. to reach the final temperature ca. 120°C .
5. Allow the reaction mixture to cool to room temperature, and extract the product into diethyl ether (10 ml) on a filtering funnel.
6. Remove the solvent by rotary evaporation and purify the product by column chromatography; yield > 70%.



## 7.2.8. 1,2-Diphenyl-ethane-1,2-dione (benzil)

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

2-Hydroxy-1,2-diphenyl ethanone (Benzoin)	0.21 g, 1.0 mmol	may act as an irritant, or be harmful
Oxone®	1.54 g, 2.5 mmol	corrosive to the eyes, skin, nose, and throat due to its acidity and oxidizing properties, and may cause allergic reactions in sensitive individuals
Aluminium oxide	2.0 g	harmful by inhalation or ingestion, irritate eyes or skin
Water	0.10 ml	non-hazardous

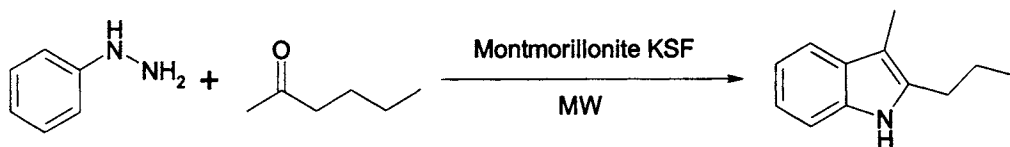
**Method [76]**

1. To a clean reaction vessel add aluminium oxide (2.0 g), 2-hydroxy-1,2-diphenyl ethanone (benzoin) (0.21 g, 1.0 mmol), Oxone® (1.54 g, 2.5 mmol), and water (0.10 ml).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).

- Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 10 min. to reach the final temperature ca. 80°C .
- Allow the reaction mixture to cool to room temperature, and extract the product into dichloromethane (3 x 15 ml) on a filtering funnel.
- Remove the solvent by rotary evaporation to obtain pure product; m.p. 94-95°C , yield > 75%.

### 7.2.9. 3-Methyl-2-propyl-1H-indole

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

#### Materials

Phenylhydrazine	1.1 g, 10 mmol	corrosive, harmful if swallowed, suspected carcinogen harmful if swallowed, inhaled or absorbed through skin, eye, skin and respiratory irritant, repeated or prolonged exposure may cause neurotoxic effects avoid contact with skin and eyes
Hexan-2-one (Butyl methyl ketone)	1.0 g, 10 mmol	
Montmorillonite KSF	3 g	

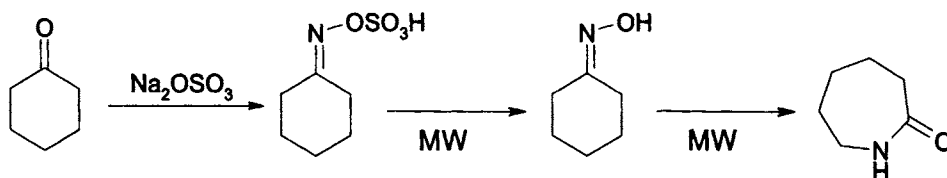
#### Method [77]

- To a clean reaction vessel add montmorillonite KSF (3.0 g), phenylhydrazine (1.1 g, 10 mmol), and butyl methyl ketone (1.0 g, 10 mmol).

2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 10 min. to reach the final temperature ca. 150°C .
5. Allow the reaction mixture to cool to room temperature, and extract the product into dichloromethane (3 x 15 ml) on a filtering funnel.
6. Remove the solvent by rotary evaporation to obtain pure product; yield > 70%.

#### 7.2.10. Azepan-2-one ( $\epsilon$ -caprolactam)

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

#### Materials

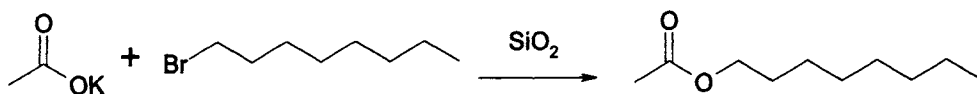
Cyclohexanone	0.25 g, 2.5 mmol	eye, skin and respiratory irritant, may cause dermatitis corrosive, danger of cumulative effects, causes burns
Hydroxylamine- <i>O</i> -sulphonic acid	0.34 g, 3.0 mmol	
Water	0.040 g	non-hazardous
Silica gel	2.0 g	harmful if inhaled, irritant, chronic exposure to the dust may be very harmful

**Method [78]**

1. To a clean reaction vessel add silica gel (2.0 g), and cyclohexanone (1.1 g, 10 mmol) then stir the mixture for 10 s with a spatula.
2. Add slowly and carefully hydroxylamine-*O*-sulphonic acid (0.34 g, 3.0 mmol) to the reaction mixture. It is possible to observe that water is released from the mixture.
3. Add another portion of water (0.040 g) to the reaction mixture then stir for 10 s with a spatula.
4. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
5. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 10 min. to reach the final temperature ca. 110°C .
6. Allow the reaction mixture to cool to room temperature, and extract the product into acetone and remove the solvent by rotary evaporation.
7. Dissolve the solid with water, neutralize the solution with an aqueous solution of sodium hydroxide (5% solution), and extract with dichloromethane.
8. Remove the solvent by rotary evaporation to obtain the product as a white solid; m.p.70-72°C , yield > 70%.

**7.2.11. Octyl acetate**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

### Materials

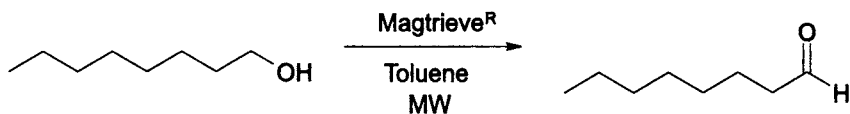
Potassium acetate	0.20 g, 2.0 mmol	may cause mild irritation to the respiratory tract, may cause mild skin irritation and redness
1-Bromooctane	1.7 g, 8.8 mmol	eye and skin irritant, may be harmful
Silica gel	0.8 g	harmful if inhaled, irritant, chronic exposure to the dust may be very harmful

### Method [79]

1. To a clean reaction vessel add silica gel (0.8 g), potassium acetate (0.20 g, 2.0 mmol), and 1-bromooctane (1.7 g, 8.8 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 10 min. to reach the final temperature ca. 125°C .
5. Allow the reaction mixture to cool to room temperature, and extract the product into dichloromethane and remove the solvent by rotary evaporation.
6. Purify the product by Kugelrohr distillation; b.p. 211°C , yield > 70%.

#### 7.2.12. Octanal

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



### Equipment

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
Reaction vessel (100 ml round-bottomed flask)  
Long-neck adapter (Figure 4.1)  
Reflux condenser

**Materials**

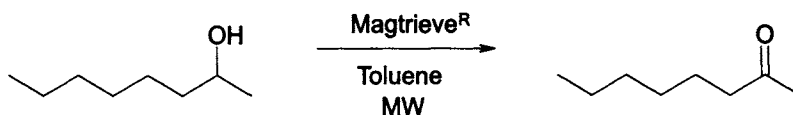
Octyl alcohol	1.0 g, 7.7 mmol	flammable, eye and skin irritant, may be harmful by ingestion or inhalation
Magtrieve™	5.0 g	none data available
Toluene	15 ml	highly flammable, toxic by inhalation, ingestion or by absorption through skin, serious irritant, experimental teratogen

**Method [80]**

1. To a round-bottomed flask (100 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add toluene (15 ml), 1-octanol (1.0 g, 7.7 mmol), and Magtrieve™ (5.0 g).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture and reflux it for 20 min. whilst stirring.
4. Allow the reaction mixture to cool to room temperature, and remove Magtrieve™ with a magnet.
5. Concentrate the solution by rotary evaporation then purify the product by Kugelrohr distillation; b.p. 69-70°C /mmHg, yield > 75%.

**7.2.13. Octan-2-one**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
 Reaction vessel (100 ml round-bottomed flask)  
 Long-neck adapter (Figure 4.1)  
 Reflux condenser

**Materials**

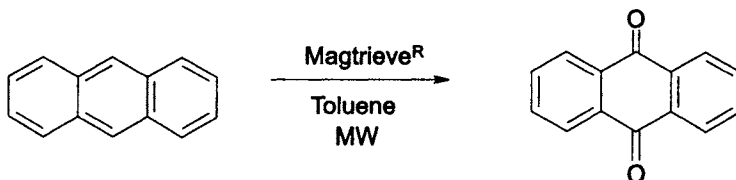
2-Octanol	1.0 g, 7.7 mmol	may be harmful by inhalation, ingestion or through skin contact, severe eye irritant
Magtrieve™	5.0 g	none data available
Toluene	15 ml	highly flammable, toxic by inhalation, ingestion or by absorption through skin, serious irritant, experimental teratogen

**Method [80]**

1. To a round-bottomed flask (100 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add toluene (15 ml), 2-octanol (1.0 g, 7.7 mmol), and Magtrieve™ (5.0 g).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture and reflux it for 25 min. whilst stirring.
4. Allow the reaction mixture to cool to room temperature, and remove Magtrieve™ with a magnet.
5. Concentrate the solution by rotary evaporation then purify the product by Kugelrohr distillation; b.p. 175-177°C, yield > 75%.

**7.2.14. Anthraquinone**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
 Reaction vessel (100 ml round-bottomed flask)  
 Long-neck adapter (Figure 4.1)  
 Reflux condenser

**Materials**

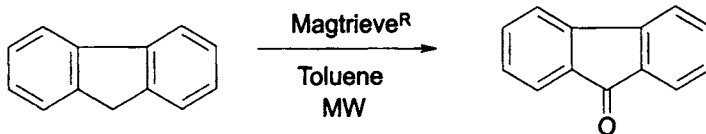
Anthracene	1.1 g, 6.0 mmol	harmful by inhalation or ingestion, may be harmful in contact with skin, suspected carcinogen
Magtrieve™	5.3 g	none data available
Toluene	30 ml	highly flammable, toxic by inhalation, ingestion or by absorption through skin, serious irritant, experimental teratogen

**Method [81]**

1. To a round-bottomed flask (100 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add toluene (15 ml), anthracene (1.1 g, 6.0 mmol), and Magtrieve™ (5.3 g).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture and reflux it for 60 min. whilst stirring.
4. Allow the reaction mixture to cool to room temperature, and remove Magtrieve™ with a magnet.
5. Concentrate the solution by rotary evaporation then purify the product by recrystallization from toluene; b.p. 284-286°C, yield > 70%.

**7.2.15. 9-Fluorenone**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
 Reaction vessel (100 ml round-bottomed flask)  
 Long-neck adapter (Figure 4.1)  
 Reflux condenser



## Materials

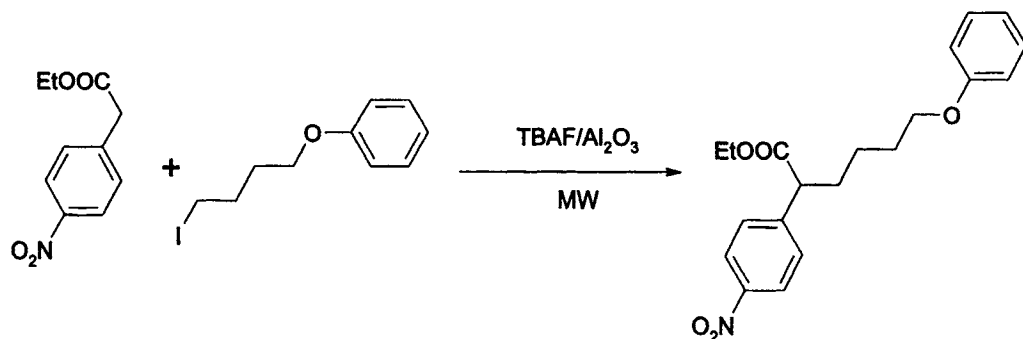
Fluorene	1.1 g, 6.0 mmol	irritant
Magtrieve™	5.3 g	none data available
Toluene	30 ml	highly flammable, toxic by inhalation, ingestion or by absorption through skin, serious irritant, experimental teratogen

### Method [81]

1. To a round-bottomed flask (100 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add toluene (15 ml), 9H-fluorene (1.1 g, 6.0 mmol), and Magtrieve™ (5.3 g).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture and reflux it for 60 min. whilst stirring.
4. Allow the reaction mixture to cool to room temperature, and remove Magtrieve™ with a magnet.
5. Concentrate the solution by rotary evaporation then purify the product by recrystallization from ethanol; m.p. 46-48°C, yield > 50%.

#### 7.2.16. 2-(4-Nitrophenyl)-6-phenoxyhexanoic acid ethyl ester

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

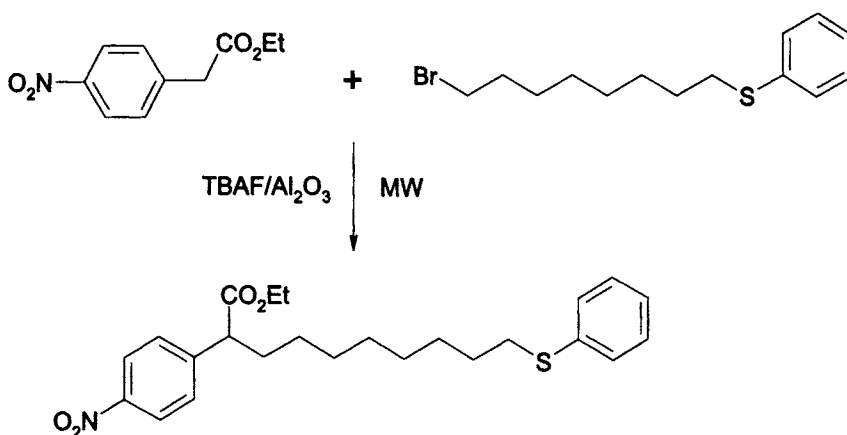
Ethyl 4-nitrophenylacetate	0.42 g, 2.0 mmol	avoid contact with skin and eyes
4-Iodobutoxybenzene	0.55 g, 2.0 mmol	none data available
Tetrabutylammonium fluoride	0.57 g, 2.2 mmol	corrosive, causes burns
Aluminium oxide	3.8 g	harmful by inhalation or ingestion, irritate eyes or skin

**Method [82]**

1. To a clean, dry reaction vessel add tetrabutylammonium fluoride on aluminium oxide (15 wt. %, 3.8 g, 2.2 mmol), ethyl 4-nitrophenylacetate (0.42 g, 2.0 mmol), and 4-iodobutoxybenzene (0.55 g, 2.0 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture up to 120°C for 10 min.
5. Allow the reaction mixture to cool to room temperature, and extract into diethyl ether (2 x 30 ml) a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, concentrate the solution by rotary evaporation.
7. Remove unreacted starting material by Kugelrohr distillation < 160°C / 2 mmHg.
8. Purified the product by column chromatography (ethyl acetate/hexane 1:4, silica gel); yield > 50%.

## 7.2.17. 2-(4-Nitrophenyl)-10-phenylsulfanyl-decanoic acid ethyl ester

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

Ethyl 4-nitrophenylacetate	0.42 g, 2.0 mmol	avoid contact with skin and eyes
8-Bromooctylsulfanylbenzene	0.60 g, 2.0 mmol	none data available
Tetrabutylammonium fluoride	0.57 g, 2.2 mmol	corrosive, causes burns
Aluminium oxide	3.8 g	harmful by inhalation or ingestion, irritate eyes or skin

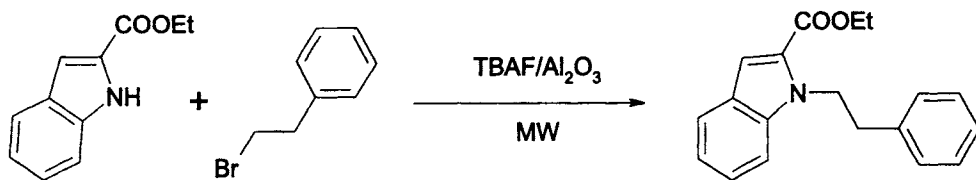
**Method [82]**

1. To a clean, dry reaction vessel add tetrabutylammonium fluoride on aluminium oxide (15 wt. %, 3.8 g, 2.2 mmol), ethyl 4-nitrophenylacetate (0.42 g, 2.0 mmol), and 8-bromooctylsulfanylbenzene (0.60 g, 2.0 mmol).

2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture up to 120°C for 10 min.
5. Allow the reaction mixture to cool to room temperature, and extract into diethyl ether (2 x 30 ml) a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, concentrate the solution by rotary evaporation.
7. Remove unreacted starting material by Kugelrohr distillation < 160°C /2 mmHg.
8. Purified the product by column chromatography (ethyl acetate/hexane 1:4, silica gel); yield > 50%.

#### 7.2.18. 1-Phenethylindole-2-carboxylic acid ethyl ester

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

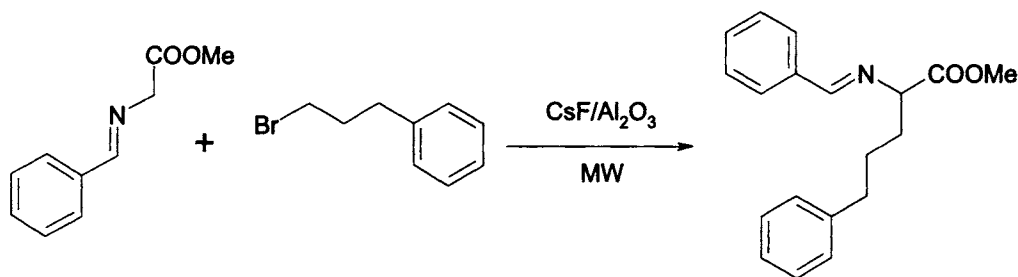
Ethyl indole-2-carboxylate	0.38 g, 2.0 mmol	<b>avoid contact with skin and eyes harmful, harmful if swallowed, irritating to eyes, respiratory system and skin</b>
(2-Bromoethyl)benzene	0.37 g, 2.0 mmol	
Tetrabutylammonium fluoride	0.57 g, 2.2 mmol	<b>corrosive, causes burns</b>
Aluminium oxide	3.8 g	<b>harmful by inhalation or ingestion, irritate eyes or skin</b>

**Method [82]**

1. To a clean, dry reaction vessel add tetrabutylammonium fluoride on aluminium oxide (15 wt. %, 3.8 g, 2.2 mmol), ethyl indole-2-carboxylate (0.38 g, 2.0 mmol), and 2-bromoethylbenzene (0.37 g, 2.0 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture up to 120°C for 10 min.
5. Allow the reaction mixture to cool to room temperature, and extract into diethyl ether (2 x 30 ml) a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, concentrate the solution by rotary evaporation.
7. Remove unreacted starting material by Kugelrohr distillation < 130°C /5 mmHg.
8. Purified the product by preparative TLC chromatography (ethyl acetate/hexane 1:9, silica gel); yield > 20%.

## 7.2.19. 5-Phenyl-2-((1-phenylmethylidene)amino)pentanoic acid methyl ester

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

((1-Phenyl-methylidene)amino)acetic acid methyl ester	0.35 g, 2.0 mmol	none data available
(3-Bromopropyl)benzene	0.40 g, 2.0 mmol	irritant, irritating to eyes, respiratory system and skin
Cesium fluoride	0.33 g, 2.2 mmol	toxic, toxic by inhalation, in contact with skin and if swallowed, causes burns
Aluminium oxide	0.80 g	harmful by inhalation or ingestion, irritate eyes or skin

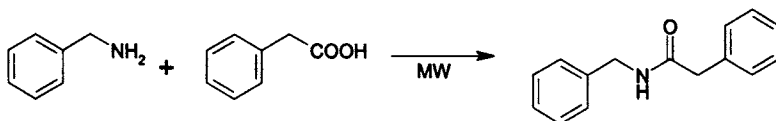
**Method [82]**

1. To a clean, dry reaction vessel add cesium fluoride on aluminium oxide (40 wt. %, 1.1 g, 2.2 mmol), ((1-phenyl-methylidene)amino)acetic acid methyl ester (0.35 g, 2.0 mmol), and 3-bromopropylbenzene (0.40 g, 2.0 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.

3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture up to 120°C for 10 min.
5. Allow the reaction mixture to cool to room temperature, and extract into diethyl ether (2 x 30 ml) a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, concentrate the solution by rotary evaporation.
7. Purified the product by preparative TLC chromatography (ethyl acetate/hexane 1:9, silica gel); yield > 20%.

### 7.2.20. N-Benzylphenylacetamide

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Mechanical stirrer

#### Materials

Benzylamine	0.32 g, 3.0 mmol	harmful if swallowed or inhaled, eye contact may lead to permanent damage
Phenylacetic acid	1.36 g, 10 mmol	harmful by ingestion, inhalation or through skin contact, severe eye irritant, skin and respiratory irritant, may act as a teratogen

**Method [83]**

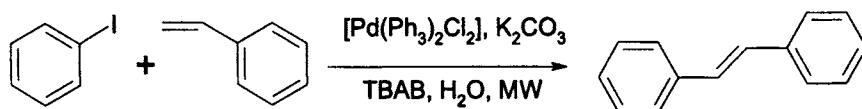
1. To a clean, dry reaction vessel add benzylamine (0.32 g, 3.0 mmol) and phenylacetic acid (1.36 g, 10 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and place the mechanical stirrer (Figure 4.4b).
4. Rotating the reaction vessel (if possible), heat the mixture to 150°C for 30 min.
5. Allow the reaction mixture to cool to room temperature, and extract with chloroform (2 x 20 ml) on a filtering funnel.
6. Wash the extract with a solution of hydrochloric acid (2 M solution, 50 ml) then sodium bicarbonate (5% solution, 50 ml) and concentrate the solution by rotary evaporation.
7. Purify the crude product by washing it with pentane; m.p. 118-129°C , yield > 80%.



## 7.3. Solvent-free phase transfer catalysis (PTC) reactions

7.3.1. *trans*-1,2-Diphenylethylene (*trans*-stilbene)

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

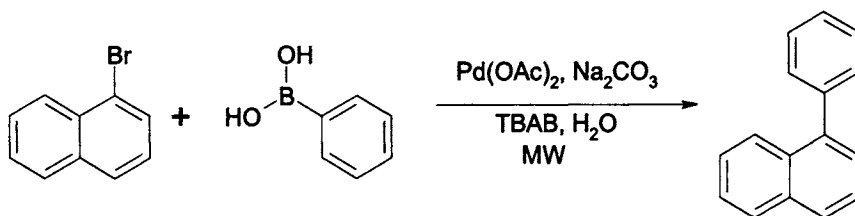
Iodobenzene	2.04 g, 10 mmol	harmful by inhalation, ingestion, by skin contact, may cause blisters, may be carcinogenic
Styrene	1.56 g, 15 mmol	toxic, carcinogen, mutagen, lachrymator, harmful by inhalation, ingestion and through skin absorption
Tetrabutylammonium bromide (TBAB)	0.32 g, 1.0 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
Bis(triphenylphosphine)-palladium(II) dichloride	35 mg, 0.050 mmol	avoid contact with skin and eyes
Potassium carbonate	4.14 g, 30 mmol	may seriously irritate respiratory system and eyes, skin irritant
Water	10 ml	

**Method [84]**

1. To a clean reaction vessel add iodobenzene (2.04 g, 10 mmol), styrene (1.56 g, 15 mmol), TBAB (0.32 g, 1.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (35 mg, 0.050 mmol), potassium carbonate (4.14 g, 30 mmol), and water (10 ml).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture with 30% power of the reactor for 10 min. to reach the final temperature: 110°C .
5. Allow the reaction mixture to cool to room temperature, add dilute HCl to acidify the reaction mixture and extract into diethyl ether (3 x 20 ml) in a separating funnel.
6. Dry the extract with magnesium sulfate filter under gravity, and concentrate the solution by rotary evaporation.
7. Purify the product by column chromatography (petroleum ether/ethyl acetate 16:1, silica gel) and recrystallize from ethanol; m.p. 123-125°C , yield > 70%.

**7.3.2. 1-Phenyl-naphthalene**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

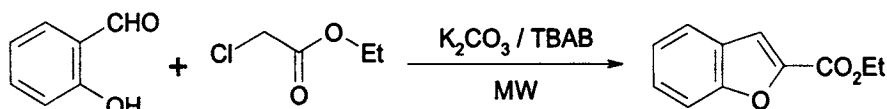
1-Bromonaphthalene	0.42 g, 2.0 mmol	may be harmful if swallowed or inhaled, may cause irritation to skin, eyes, and respiratory tract
Phenyl boronic acid	0.25 g, 2.0 mmol	may be fatal if inhaled, harmful if absorbed through skin, material is extremely destructive to the tissue of the eyes and skin
Tetrabutylammonium bromide (TBAB)	0.16 g, 0.50 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
Sodium carbonate	0.63 g, 6.0 mmol	eye and respiratory irritant
Palladium acetate (II)	2.0 mg, $8.9 \cdot 10^{-6}$ mmol	avoid contact with skin and eyes
Water	4.0 ml	non-hazardous

**Method [85]**

1. To a clean, dry reaction vessel add sodium carbonate (0.63 g, 6.0 mmol), 1-bromonaphthalene (0.42 g, 2.0 mmol), phenyl boronic acid (0.25 g, 2.0 mmol), TBAB (0.16 g, 0.50 mmol), palladium acetate (II) (2.0 mg,  $8.9 \cdot 10^{-6}$  mmol) and water (4 ml).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture with 20% power of the reactor for 10 min. to reach the final temperature ca. 110°C .
5. Allow the reaction mixture to cool to room temperature, and extract with dichloromethane (3 x 30 ml) in a separating funnel.
6. Dry the extract with magnesium sulfate filter under gravity, and concentrate the solution by rotary evaporation; b.p. 324-325°C , yield > 60%.

### 7.3.3. Benzofuran-2-carboxylic acid ethyl ester

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

#### Materials

2-Hydroxybenzaldehyde (Salicylaldehyde)	0.61 g, 5.0 mmol	harmful if swallowed, inhaled or absorbed through skin, irritant
Ethyl chloroacetate	0.108 g, 10 mmol	moisture sensitive, harmful if swallowed, irritant
Tetrabutylammonium bromide (TBAB)	0.16 g, 0.50 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
Potassium carbonate	2.70 g, 20 mmol	may seriously irritate respiratory system and eyes, skin irritant

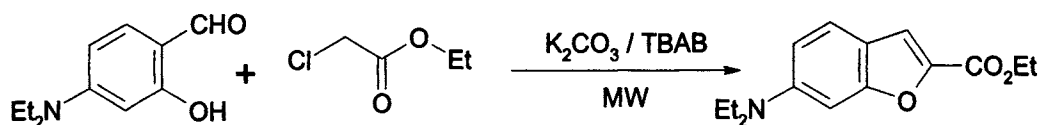
#### Method [86]

1. To a clean, dry reaction vessel add 2-hydroxybenzaldehyde (salicylaldehyde) (0.61 g, 5.0 mmol), ethyl chloroacetate (0.108 g, 10 mmol), potassium carbonate (2.70 g, 20 mmol), and TBAB (0.16 g, 0.50 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture with 20% power of the reactor for 10 min. to reach the final temperature: 120°C .

5. Allow the reaction mixture to cool to room temperature, and extract with dichloromethane (3 x 30 ml) on a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, and concentrate the solution by rotary evaporation.
7. Purify the product by column chromatography (cyclohexane/methyl chloride 8:2, silica gel) to obtain it as a colorless oil, yield > 60%.

#### 7.3.4. 6-Diethylamino-benzofuran-2-carboxylic acid ethyl ester

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)  
 Reaction vessel (Figure 4.2b)  
 Adapter (Figure 4.2f)  
 Cold finger

#### Materials

4-Diethylamino-2-hydroxybenzaldehyde	0.96 g, 5.0 mmol	irritant, irritating to eyes, respiratory system and skin moisture sensitive, harmful if swallowed, irritant
Methyl chloroacetate	0.108 g, 10 mmol	
Tetrabutylammonium bromide (TBAB)	0.16 g, 0.50 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
Potassium carbonate	2.70 g	

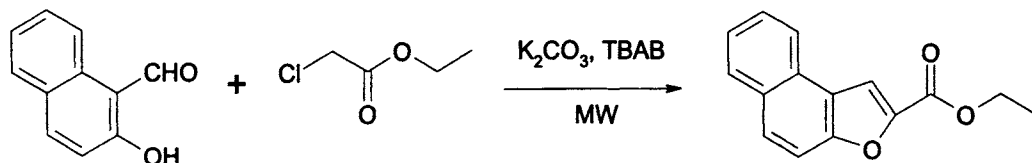
20 mmol may seriously irritate respiratory system and eyes, skin irritant

**Method [86]**

1. To a clean, dry reaction vessel add 4-diethylamino-2-hydroxybenzaldehyde (0.96 g, 5.0 mmol), ethyl chloroacetate (0.108 g, 10 mmol), potassium carbonate (2.70 g, 20 mmol), and TBAB (0.16 g, 0.50 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture with 20% power of the reactor for 10 min. to reach the final temperature ca. 120 °C .
5. Allow the reaction mixture to cool to room temperature, and extract with dichloromethane (3 x 30 ml) on a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, and concentrate the solution by rotary evaporation.
7. Purify the product by column chromatography (cyclohexane/methyl chloride 8:2, silica gel) to obtain it as a red oil, yield > 60%.

**7.3.5. Naphtho[2,1-b]furan-2-carboxylic acid ethyl ester**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

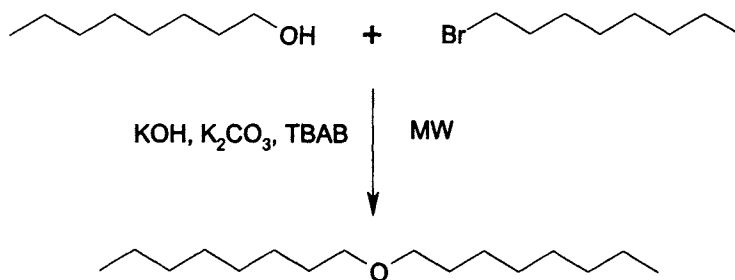
2-Hydroxy-1-naphthaldehyde	0.86 g, 5.0 mmol	avoid contact with skin and eyes flammable, harmful if swallowed, irritant
Ethyl chloroacetate	1.2 g, 10 mmol	flammable, harmful if swallowed, irritant
Tetrabutylammonium bromide (TBAB)	0.16 g, 0.50 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
Potassium carbonate	2.70 g, 20 mmol	may seriously irritate respiratory system and eyes, skin irritant

**Method [86]**

1. To a clean, dry reaction vessel add 2-hydroxy-1-naphthaldehyde (0.86 g, 5.0 mmol), ethyl chloroacetate (1.2 g, 10 mmol), potassium carbonate (2.70 g, 20 mmol), and TBAB (0.16 g, 0.50 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture with 30% power of the reactor for 10 min. to reach final temperature ca. 150°C .
5. Allow the reaction mixture to cool to room temperature, and extract with dichloromethane (3 x 30 ml) on a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, and concentrate the solution by rotary evaporation.
7. Purify the product by column chromatography (cyclohexane/methyl chloride 8:2, silica gel) to obtain it as a white solid; m.p. 85-88°C , yield > 60%.

## 7.3.6. Dioctyl ether

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

Octyl alcohol	0.65 g, 5.0 mmol	flammable, eye and skin irritant, may be harmful by ingestion or inhalation
1-Bromooctane	1.2 g, 6.0 mmol	eye and skin irritant, may be harmful
Tetrabutylammonium bromide (TBAB)	0.16 g, 0.50 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
Potassium carbonate	2.70 g, 20 mmol	may seriously irritate respiratory system and eyes, skin irritant
Potassium hydroxide	1.1 g, 20 mmol	very hygroscopic, harmful by ingestion, inhalation and in contact with skin, if the solid or solution comes into contact with the eyes, serious eye damage may result

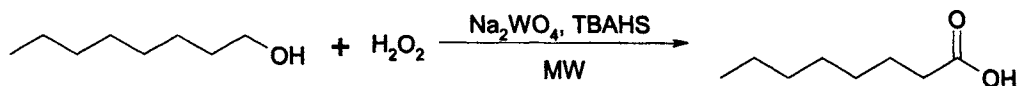


**Method [87]**

1. To a clean, dry reaction vessel add octyl alcohol (0.65 g, 5.0 mmol), 1-bromooctane (1.2 g, 6.0 mmol), potassium carbonate (2.70 g, 20 mmol), finely powdered potassium hydroxide (1.1 g, 20 mmol), and TBAB (0.16 g, 0.50 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture with 30% power of the reactor for 10 min. to reach the final temperature ca. 150°C .
5. Allow the reaction mixture to cool to room temperature, and extract with THF (2 x 30 ml) on a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, and concentrate the solution by rotary evaporation.
7. Purify the product by Kugelrohr distillation; b.p. 284-286°C , yield > 70%.

**7.3.7. Octanoic acid**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
 Reaction vessel (50 ml round-bottomed flask)  
 Long-neck adapter (Figure 4.1)  
 Reflux condenser

**Materials**

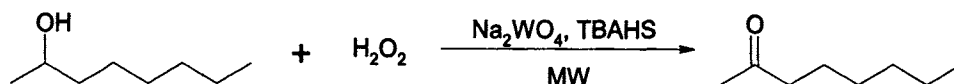
Octyl alcohol	2.6 g, 20 mmol	flammable, eye and skin irritant, may be harmful by ingestion or inhalation
Hydrogen peroxide (30% solution)	11.3 g, 100 mmol	corrosive, causes burns, after contact with skin wash immediately with plenty of water
Sodium tungstate dihydrate	0.26 g, 0.79 mmol	may act as an irritant
Tetrabutylammonium hydrogen sulfate (TBAHS)	0.27 g, 0.80 mmol	harmful, harmful if swallowed
Sodium tungstate dihydrate	0.26 g, 0.79 mmol	may act as an irritant

**Method [88]**

1. To a round-bottomed flask (50 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add octyl alcohol (2.6 g, 20 mmol), hydrogen peroxide (30% solution) (11.3 g, 100 mmol), sodium tungstate dihydrate (0.26 g, 0.79 mmol), and TBAHS (0.27 g, 0.80 mmol).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture to 90°C for 20 min. whilst stirring.
4. Allow the reaction mixture to cool to room temperature, add an aqueous solution of sodium carbonate (20% w/w, 50 ml), and extract with ethyl acetate (2 x 20 ml).
5. Acidify the aqueous phase with diluted hydrochloric acid, and extract it again with ethyl acetate (2 x 20 ml).
6. Combine the organic phases, dry over magnesium sulfate, filter under gravity, and concentrate the solution by rotary evaporation.
7. Purify the product by Kugelrohr distillation; b.p. 237°C, yield > 70%.

## 7.3.8. Octan-2-one

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
 Reaction vessel (50 ml round-bottomed flask)  
 Long-neck adapter (Figure 4.1)  
 Reflux condenser

**Materials**

2-Octanol	1.9 g, 15 mmol	may be harmful by inhalation, ingestion or through skin contact, severe eye irritant
Hydrogen peroxide (30% solution)	2.72 g, 24 mmol	corrosive, causes burns, after contact with skin wash immediately with plenty of water
Tetrabutylammonium hydrogen sulfate (TBAHS)	0.20 g, 0.59 mmol	harmful, harmful if swallowed
Sodium tungstate dihydrate	0.19 g, 0.58 mmol	may act as an irritant

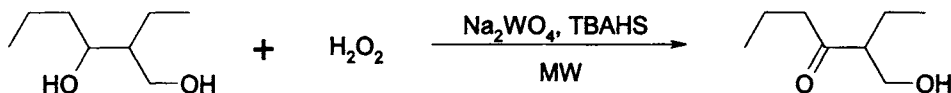
**Method [88]**

1. To a round-bottomed flask (50 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add 2-octanol (1.9 g, 20 mmol), hydrogen peroxide (30% solution) (2.72 g, 24 mmol), sodium tungstate dihydrate (0.19 g, 0.58 mmol), and TBAHS (0.20 g, 0.59 mmol).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture to 100°C for 10 min. whilst stirring.

4. Allow the reaction mixture to cool to room temperature, and extract with ethyl acetate (2 x 30 ml) in a separating funnel.
5. Dry the organic phase over magnesium sulfate, filter under gravity, and concentrate the solution by rotary evaporation.
6. Purify the product by Kugelrohr distillation; b.p. 173°C , yield > 80%.

### 7.3.9. 3-Hydroxymethylheptan-4-one

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
 Reaction vessel (50 ml round-bottomed flask)  
 Long-neck adapter (Figure 4.1)  
 Reflux condenser

#### Materials

2-Ethylhexane-1,3-diol	2.6 g, 20 mmol	none data available
Hydrogen peroxide (30% solution)	2.72 g, 24 mmol	corrosive, causes burns, after contact with skin wash immediately with plenty of water
Tetrabutylammonium hydrogen sulfate (TBAHS)	0.20 g, 0.59 mmol	harmful, harmful if swallowed
Sodium tungstate dihydrate	0.19 g, 0.58 mmol	may act as an irritant

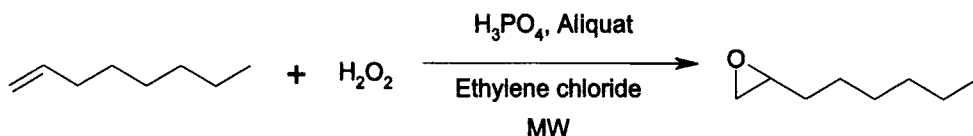
#### Method

1. To a round-bottomed flask (50 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add 2-ethylhexane-1,3-diol (2.6 g, 20 mmol), hydrogen peroxide (30% solution) (2.72 g, 24 mmol), sodium tungstate dihydrate (0.19 g, 0.58 mmol), and TBAHS (0.20 g, 0.59 mmol).

2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture to 100°C for 10 min. whilst stirring.
4. Allow the reaction mixture to cool to room temperature, and extract with ethyl acetate (2 x 30 ml) in a separating funnel.
5. Dry the organic phase over magnesium sulfate, filter under gravity, and concentrate the solution by rotary evaporation.
6. Purify the product by Kugelrohr distillation; yield > 80%.

#### 7.3.10. 1,2-Epoxydodecene

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
 Reaction vessel (50 ml round-bottomed flask)  
 Long-neck adapter (Figure 4.1)  
 Reflux condenser

#### Materials

1-Dodecene	4.7 g, 28 mmol	harmful if swallowed or inhaled, eye, skin and respiratory irritant corrosive, causes burns, after contact with skin wash immediately with plenty of water
Hydrogen peroxide (8% solution)	4.5 g, 35 mmol	

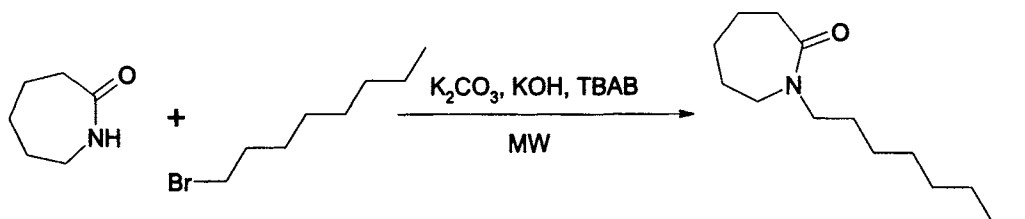
Aliquat <sup>TM</sup>	0.10 g, 0.25 mmol	<b>harmful if swallowed or inhaled, eye, skin and respiratory irritant</b>
Sodium tungstate dihydrate	0.14 g, 0.72 mmol	<b>may act as an irritant</b>
Phosphoric acid (40% solution)	0.17 g, 1.72 mmol	<b>corrosive - causes burns, harmful if swallowed and in contact with skin, may be harmful through inhalation, very destructive of mucous membranes, respiratory tract, eyes and skin</b>
Ethylene chloride	2.1 ml	<b>highly flammable, probable human carcinogen, causes liver damage, mutagen, toxic, may cause systemic effects, narcotic</b>

### Method [89]

1. To a round-bottomed flask (50 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add ethylene chloride (2.1 ml), Aliquat<sup>TM</sup> (0.10 g, 0.25 mmol), sodium tungstate dihydrate (0.14 g, 0.72 mmol), phosphoric acid (40% solution) (0.17 g, 1.72 mmol), and adjust pH of the solution to ca. 1.6 with a diluted sulfuric acid (30% solution).
2. Add 1-dodecene (4.7 g, 28 mmol) to the reaction flask, and then place it in the cavity of multi-mode microwave reactor, attach the long-neck adapter together with the reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture at 70°C whilst stirring, and add hydrogen peroxide (8% solution) in 15 min. intervals so that the total reaction time is 1h.
4. Allow the reaction mixture to cool to room temperature, and separate the phases, and extract the aqueous phase with ethylene chloride (2 x 10 ml).
5. Combine the organic phases, dry over magnesium sulfate, filter under gravity, and concentrate the solution by rotary evaporation.
6. Purify the product by Kugelrohr distillation; b.p. 123-124°C /mmHg, yield > 70%.

## 7.3.11. 1-Octyl-azepan-2-one (N-Octylcaprolactam)

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

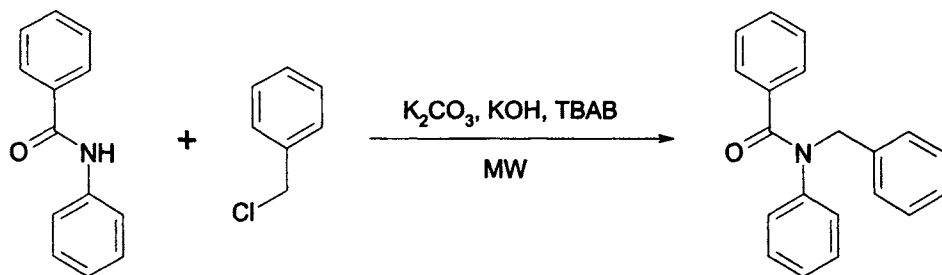
$\epsilon$ -Caprolactam	0.56 g, 5.0 mmol	hygroscopic, harmful if swallowed, inhaled or absorbed through the skin, skin and eye irritant
1-Bromooctane	1.4 g, 7.5 mmol	eye and skin irritant, may be harmful
Tetrabutylammonium bromide (TBAB)	0.16 g, 0.50 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
Potassium carbonate	2.70 g, 20 mmol	may seriously irritate respiratory system and eyes, skin irritant
Potassium hydroxide	1.1 g, 20 mmol	very hygroscopic, harmful by ingestion, inhalation and in contact with skin, if the solid or solution comes into contact with the eyes, serious eye damage may result

**Method [90]**

1. To a clean, dry reaction vessel add  $\epsilon$ -caprolactam (0.56 g, 5.0 mmol), 1-bromooctane (1.4 g, 7.5 mmol), potassium carbonate (2.70 g, 20 mmol), finely powdered potassium hydroxide (1.1 g, 20 mmol), and TBAB (0.16 g, 0.50 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture up to 150-160°C for 10 min.
5. Allow the reaction mixture to cool to room temperature, and extract into dichloromethane (2 x 30 ml) a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, concentrate the solution by rotary evaporation.
7. Purify the product by Kugelrohr distillation; b.p. 155-160°C /5 mmHg, yield > 70%.

**7.3.12. N-Benzyl-N-phenylbenzamide**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger



**Materials**

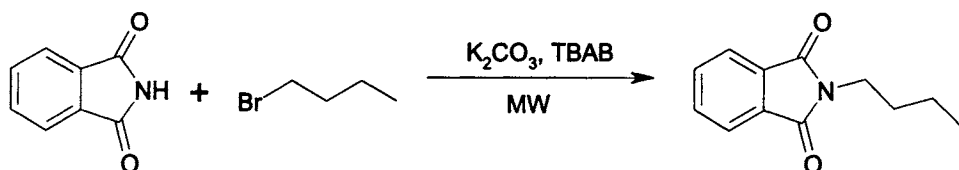
Benzanilide	0.98 g, 5.0 mmol	hygroscopic, harmful if swallowed, inhaled or absorbed through the skin, skin and eye irritant
Benzyl chloride	0.94 g, 7.5 mmol	toxic, probable human carcinogen, contact with the eyes may cause permanent damage, harmful by inhalation, ingestion and through skin contact
Tetrabutylammonium bromide (TBAB)	0.16 g, 0.50 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
Potassium carbonate	2.70 g, 20 mmol	may seriously irritate respiratory system and eyes, skin irritant
Potassium hydroxide	1.1 g, 20 mmol	very hygroscopic, harmful by ingestion, inhalation and in contact with skin, if the solid or solution comes into contact with the eyes, serious eye damage may result

**Method [90]**

1. To a clean, dry reaction vessel add benzanilide (0.98 g, 5.0 mmol), benzyl chloride (0.94 g, 7.5 mmol), potassium carbonate (2.70 g, 20 mmol), finely powdered potassium hydroxide (1.1 g, 20 mmol), and TBAB (0.16 g, 0.50 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture up to 150°C for 10 min.
5. Allow the reaction mixture to cool to room temperature, and extract into dichloromethane (2 x 30 ml) a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, concentrate the solution by rotary evaporation, and recrystallize the product from ethanol; m.p. 106-108°C, yield > 75%.

### 7.3.13. N-Butylphthalimide

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

#### Materials

Phthalimide	0.70 g, 4.8 mmol	suspected teratogen harmful if swallowed or inhaled, Skin, eye and respiratory irritant, liquid may burn skin or eyes
1-Bromobutane	0.82 g, 6.0 mmol	
Tetrabutylammonium bromide (TBAB)	0.15 g, 0.45 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
Potassium carbonate	2.6 g, 19 mmol	
		may seriously irritate respiratory system and eyes, skin irritant

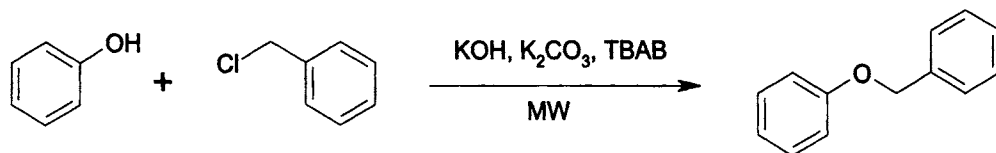
#### Method [91]

1. To a clean, dry reaction vessel add phthalimide (0.70 g, 4.8 mmol), butyl bromide (0.82 g, 6.0 mmol), potassium carbonate (2.6 g, 19 mmol), and TBAB (0.15 g, 0.45 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).

- Rotating the reaction vessel (if possible), heat the mixture up to 100-120°C for 10 min.
- Allow the reaction mixture to cool to room temperature, and extract into dichloromethane (2 x 30 ml) a filtering funnel.
- Dry the extract with magnesium sulfate filter under gravity, concentrate the solution by rotary evaporation, and purify the product by Kugelrohr distillation m.p. 32-34°C, yield > 60%.

#### 7.3.14. Benzylphenyl ether

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

#### Materials

Phenol	0.47 g, 5.0 mmol	suspected teratogen toxic, probable human carcinogen, contact with the eyes may cause permanent damage, harmful by inhalation, ingestion and through skin contact
Benzyl chloride	0.75 g, 6.0 mmol	
Tetrabutylammonium bromide (TBAB)	0.17 g, 0.50 mmol	
		harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant

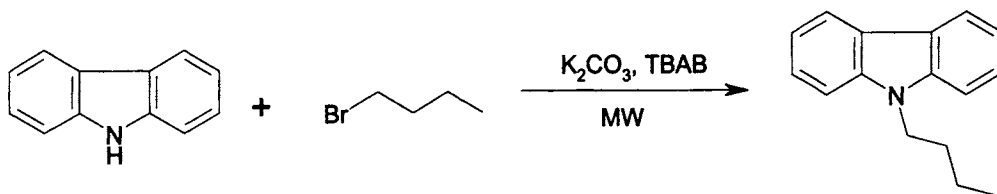
Potassium carbonate	2.8 g, 20 mmol	<b>may seriously irritate respiratory system and eyes, skin irritant very hygroscopic, harmful by ingestion, inhalation and in contact with skin, if the solid or solution comes into contact with the eyes, serious eye damage may result</b>
Potassium hydroxide	1.1 g, 20 mmol	

### Method [92]

1. To a clean, dry reaction vessel add phenol (0.47 g, 5.0 mmol), benzyl chloride (0.75 g, 6.0 mmol), potassium carbonate (2.80 g, 20 mmol), finely powdered potassium hydroxide (1.1 g, 20 mmol), and TBAB (0.17 g, 0.50 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture to 130-140°C for 10 min.
5. Allow the reaction mixture to cool to room temperature, and extract with THF (2 x 30 ml) on a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, and concentrate the solution by rotary evaporation.
7. Purify the product by recrystallization from ethanol; m.p. 39-40°C , yield > 65%.

#### 7.3.15. N-Butylcarbazole

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

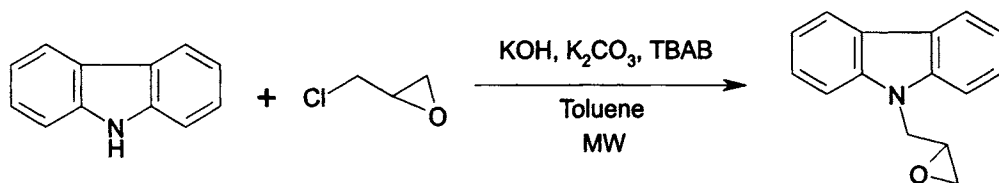
Carbazole	0.84 g, 5.0 mmol	harmful by inhalation or ingestion, may be harmful in contact with skin, suspected carcinogen
1-Bromobutane	1.0 g, 7.5 mmol	harmful if swallowed or inhaled, Skin, eye and respiratory irritant, liquid may burn skin or eyes
Tetrabutylammonium bromide (TBAB)	0.17 g, 0.50 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
Potassium carbonate	2.8 g, 20 mmol	may seriously irritate respiratory system and eyes, skin irritant

**Method [93]**

1. To a clean, dry reaction vessel add carbazole (0.84 g, 5.0 mmol), butyl bromide (1.0 g, 6.0 mmol), potassium carbonate (2.80 g, 20 mmol), finely powdered potassium hydroxide (1.1 g, 20 mmol), and TBAB (0.17 g, 0.50 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture to 120-130°C for 10 min.
5. Allow the reaction mixture to cool to room temperature, and extract with THF (2 x 30 ml) on a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, and concentrate the solution by rotary evaporation.
7. Purify the product by recrystallization from ethanol; m.p. 57-59°C, yield > 65%.

## 7.3.16. N-(2,3-Epoxypropyl)carbazole

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)

Reaction vessel (250 ml round-bottomed flask)

Long-neck adapter (Figure 4.1)

Reflux condenser

**Materials**

Carbazole	5.0 g, 30 mmol	harmful by inhalation or ingestion, may be harmful in contact with skin, suspected carcinogen
Epichlorohydrin	5.5 g, 60 mmol	flammable, poison, harmful if inhaled - may cause delayed lung damage, may be fatal if swallowed, reported as causing cancer in laboratory animals, causes burns, contact with eyes may cause permanent damage, long-term exposure may lead to liver or kidney damage
Tetrabutylammonium bromide (TBAB)	0.50 g, 1.5 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant

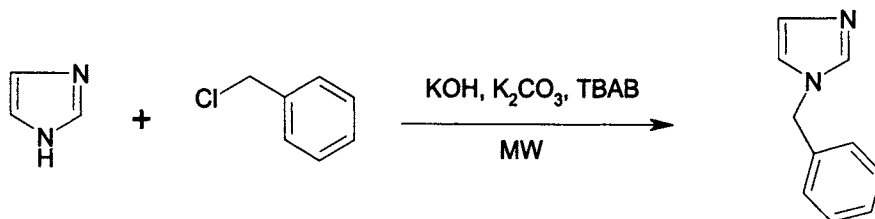
Potassium carbonate	16.7 g, 120 mmol	may seriously irritate respiratory system and eyes, skin irritant very hygroscopic, harmful by ingestion, inhalation and in contact with skin, if the solid or solution comes into contact with the eyes, serious eye damage may result
Potassium hydroxide	1.7 g, 30 mmol	
Toluene	90 ml	highly flammable, toxic by inhalation, ingestion or by absorption through skin, serious irritant, experimental teratogen

### Method [89]

1. To a round-bottomed flask (250 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add toluene (90 ml), carbazole (5.0 g, 30 mmol), epichlorohydrin (5.5 g, 60 mmol), TBAB (0.50 g, 1.5 mmol), potassium carbonate (16.7 g, 120 mmol), and finely powdered potassium hydroxide (1.7 g, 30 mmol).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser (Figure 4.1a).
3. Irradiate the reaction mixture to 105-106°C for 20 min. whilst stirring.
4. Allow the reaction mixture to cool to room temperature, filter under gravity, and rinse the inorganic solid with ethyl acetate (2 x 30 ml).
5. Combine the organic phases, dry over magnesium sulfate, filter under gravity, and concentrate the solution by rotary evaporation.
6. Recrystallize the solid from ethanol and leave it in fridge overnight to complete crystalization; m.p. 109-111°C, yield > 80%.

## 7.3.17. 1-Benzylimidazole

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

Imidazole	0.34 g, 5.0 mmol	corrosive - causes burns, harmful by ingestion or inhalation, may cause serious burns to the skin or eyes
Benzyl chloride	0.95 g, 7.5 mmol	toxic, probable human carcinogen, contact with the eyes may cause permanent damage, harmful by inhalation, ingestion and through skin contact
Tetrabutylammonium bromide (TBAB)	0.17 g, 0.50 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
Potassium carbonate	2.8 g, 20 mmol	may seriously irritate respiratory system and eyes, skin irritant



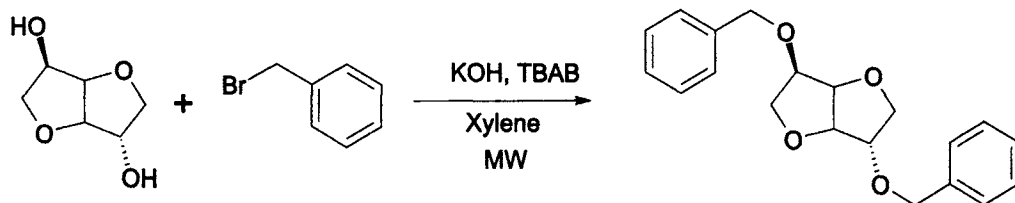
Potassium hydroxide	1.1 g, 20 mmol	<b>very hygroscopic, harmful by ingestion, inhalation and in contact with skin, if the solid or solution comes into contact with the eyes, serious eye damage may result</b>
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**Method [94]**

1. To a clean, dry reaction vessel add imidazole (0.34 g, 5.0 mmol), benzyl chloride (0.95 g, 7.5 mmol), potassium carbonate (2.80 g, 20 mmol), finely powdered potassium hydroxide (1.1 g, 20 mmol), and TBAB (0.17 g, 0.50 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), heat the mixture to 120-130°C for 10 min.
5. Allow the reaction mixture to cool to room temperature, and rinse with THF (2 x 30 ml) on a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, and concentrate the solution by rotary evaporation.
7. Purify the product by Kugelrohr distillation; b.p. 120-122°C /10 mmHg, yield > 60%.

**7.3.18. D-sorbitol 1,4:3,6-dianhydro,2,5-di-O, O-benzyl**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Mechanical stirrer

**Materials**

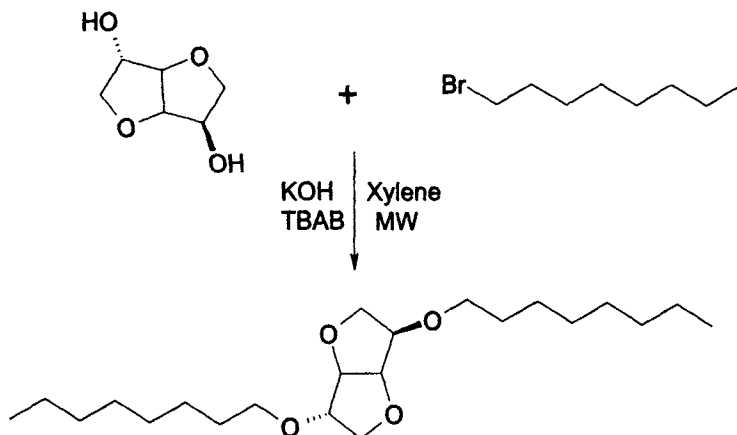
1,4:3,6-dianhydrosorbitol (isosorbide)	1.46 g, 10 mmol	avoid contact with skin and eyes
Benzyl bromide	5.1 g, 30 mmol mmol	harmful if swallowed or inhaled, Skin, eye and respiratory irritant, liquid may burn skin or eyes
Tetrabutylammonium bromide (TBAB)	0.60 g, 2.0 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
Potassium hydroxide	2.0 g, 30 mmol	very hygroscopic, harmful by ingestion, inhalation and in contact with skin, if the solid or solution comes into contact with the eyes, serious eye damage may result
Xylene	1 ml	eye, skin and respiratory irritant, may act as a narcotic

**Method [95]**

1. To a clean, dry reaction vessel add isosorbide (1.5 g, 10 mmol), benzyl bromide (5.1 g, 30 mmol), finely powdered potassium hydroxide (2.0 g, 30 mmol), xylene (1 ml), and TBAB (0.60 g, 2.0 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and place the mechanical stirrer (Figure 4.4b).
4. Rotating the reaction vessel (if possible), heat the mixture to 120-125°C for 10 min.
5. Allow the reaction mixture to cool to room temperature, and rinse with dichloromethane (2 x 30 ml) on a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, and concentrate the solution by rotary evaporation to obtain the product as a colourless oil; yield > 70%.

7.3.19. D-sorbitol 1,4:3,6-dianhydro,2,5-di-*O*,*O*-octyl

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Mechanical stirrer

**Materials**

1,4:3,6-dianhydrosorbitol (isosorbide)	1.46 g, 10 mmol	avoid contact with skin and eyes
1-Bromooctane	3.42 g, 10 mmol	eye and skin irritant, may be harmful
Tetrabutylammonium bromide (TBAB)	0.32 g, 1.0 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant

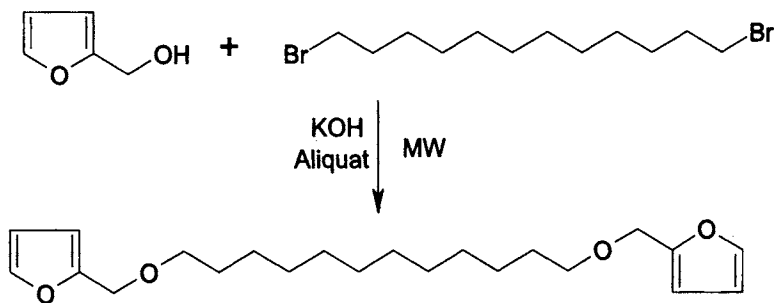
Potassium hydroxide	2.0 g, 30 mmol	<b>very hygroscopic, harmful by ingestion, inhalation and in contact with skin, if the solid or solution comes into contact with the eyes, serious eye damage may result</b>
Toluene	0.5 ml	<b>highly flammable, toxic by inhalation, ingestion or by absorption through skin, serious irritant, experimental teratogen</b>

### Method [96]

1. To a clean, dry reaction vessel add isosorbide (0.5 g, 3.4 mmol), octyl bromide (3.4 g, 10 mmol), finely powdered potassium hydroxide (2.0 g, 30 mmol), toluene (0.5 ml), and TBAB (0.32 g, 1.0 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and apply the mechanical stirrer (Figure 4.4b).
4. Rotating the reaction vessel (if possible), heat the mixture to 140°C for 5 min.
5. Allow the reaction mixture to cool to room temperature, and rinse with dichloromethane (2 x 30 ml) on a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, and concentrate the solution by rotary evaporation to obtain the product as a colourless oil; yield > 70%.

## 7.3.20. 1,12-Bis(furan-2-ylmethoxy)dodecane

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Mechanical stirrer

**Materials**

Furfuryl alcohol	1.96 g, 20 mmol	may react explosively with acids, combustible, toxic; inhalation, ingestion, or skin contact may cause severe injury or death, contact with molten substance may cause severe burns to skin and eyes, avoid any skin contact, effects of contact or inhalation may be delayed
1,12-dibromododecane	1.63 g, 10 mmol	may be harmful or act as an irritant - toxicology not fully investigated

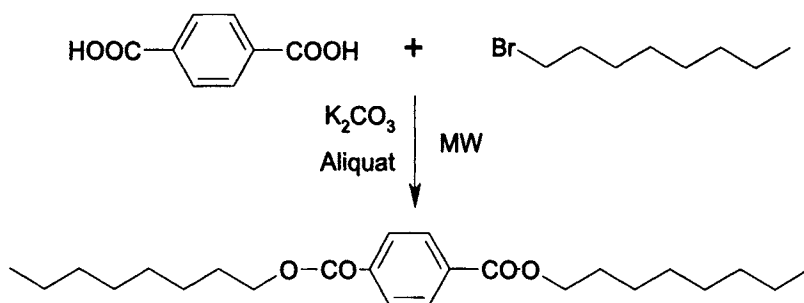
Aliquat <sup>TM</sup>	0.40 g, 1.0 mmol	<b>harmful if swallowed or inhaled, eye, skin and respiratory irritant</b>
Potassium hydroxide	1.0 g, 15 mmol	<b>very hygroscopic, harmful by ingestion, inhalation and in contact with skin, if the solid or solution comes into contact with the eyes, serious eye damage may result</b>

### Method [97]

1. To a clean, dry reaction vessel add furfuryl alcohol (1.9 g, 20 mmol), 1,12-dibromododecane (1.6 g, 5.0 mmol), finely powdered potassium hydroxide (1.0 g, 15 mmol), and Aliquat (0.40 g, 1.0 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and apply the mechanical stirrer (Figure 4.4b).
4. Rotating the reaction vessel (if possible), heat the mixture to 170°C for 10 min.
5. Allow the reaction mixture to cool to room temperature, and rinse with dichloromethane (2 x 30 ml) on a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, and concentrate the solution by rotary evaporation, and pour dropwise into methanol under intense stirring.
7. Filter the solid material under gravity and recrystallize from the mixture of acetone and water (2:1, v/v); m.p. 45-48°C, yield > 70%.

## 7.3.21. Dioctyl terephthalate

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



## Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Mechanical stirrer

## Materials

Terephthalic acid	0.83 g, 5.0 mmol	irritant
1-Bromooctane	1.93 g, 10 mmol	eye and skin irritant, may be harmful
Aliquat <sup>TM</sup>	0.40 g, 1.0 mmol	harmful if swallowed or inhaled, eye, skin and respiratory irritant
Potassium carbonate	1.4 g, 10 mmol	may seriously irritate respiratory system and eyes, skin irritant

## Method [98]

1. To a clean, dry reaction vessel add terephthalic acid (0.83 g, 5.0 mmol), octyl bromide (1.8 g, 10 mmol), potassium carbonate (1.4 g, 10 mmol), and Aliquat (0.40 g, 1.0 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and apply the mechanical stirrer (Figure 4.4b).

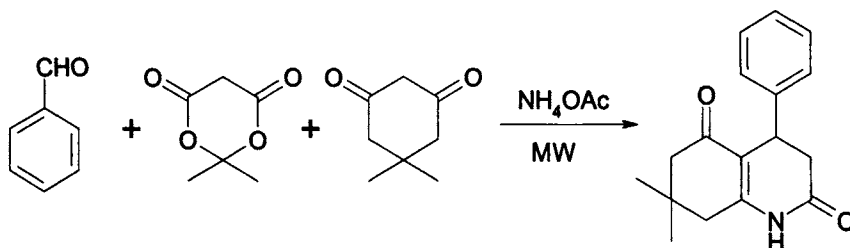
4. Rotating the reaction vessel (if possible), heat the mixture to 210-220°C for 10 min.
5. Allow the reaction mixture to cool to room temperature, and rinse with dichloromethane (2 x 30 ml) on a filtering funnel.
6. Dry the extract with magnesium sulfate filter under gravity, and concentrate the solution by rotary evaporation;
7. Recrystallize the product from ethanol; m.p. 30-32°C , yield > 70%.



## 7.4. Reactions of neat reagents

## 7.4.1. 7,7-Dimethyl-4-phenyl-4,6,7,8-tetrahydro-1H,3H-quinoline-2,5-dione

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



## Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

## Materials

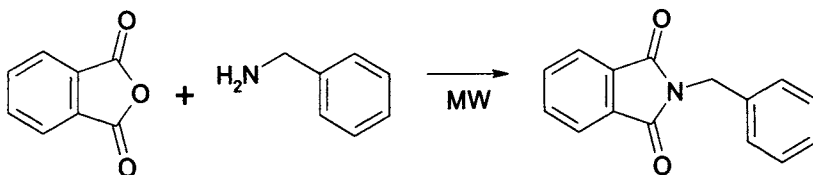
Benzaldehyde	0.53 g, 5.0 mmol	eye irritant, harmful by inhalation or ingestion, may be harmful by skin contact and cause allergic reaction
2,2-Dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid)	0.72 g, 5.0 mmol	may cause eye, skin, and respiratory tract irritation
5,5-Dimethyl-1,3-cyclohexanedione (dimedone)	0.71 g, 5.0 mmol	may be harmful or act as an irritant
Ammonium acetate	0.61 g, 8.0 mmol	may be harmful by inhalation or ingestion, irritant
Ethanol	2 ml	causes skin and eye irritation

**Method [99]**

1. To a clean reaction vessel add benzaldehyde (0.53 g, 5.0 mmol), Meldrum's acid (0.72 g, 5.0 mmol, dimedone (0.71 g, 5.0 mmol), and ammonium acetate (0.61 g, 8.0 mmol).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 10 min. to reach temperature ca. 130°C during the irradiation.
5. Allow the reaction mixture to cool to room temperature, add ethanol (2 ml), and filter the precipitated solid on a filter funnel.
6. Purify the product by further recrystallization from ethanol; yield > 60%.

**7.4.2. N-Benzyl-phthalimide**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

### Materials

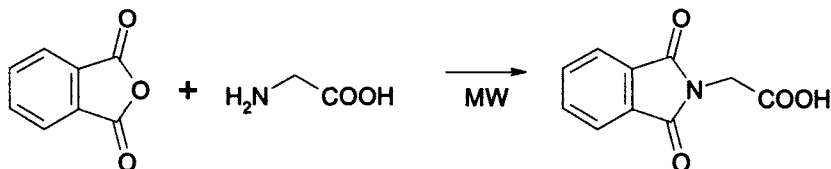
Phthalic anhydride	1.35 g, 9.2 mmol	harmful if swallowed or inhaled, skin or eye contact may cause severe irritation
Benzylamine	0.68 g, 9.2 mmol	harmful if swallowed or inhaled, eye contact may lead to permanent damage
Xylene	2 ml	eye, skin and respiratory irritant, may act as a narcotic

### Method [100]

1. To a clean reaction vessel add phthalic anhydride (1.35 g, 9.2 mmol), benzylamine (0.68 g, 9.2 mmol), and xylene (2 ml).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 50% power of the reactor for 10 min. to reach temperature ca. 150°C during the irradiation.
5. Allow the reaction mixture to cool to room temperature and recrystallize the crude product from ethanol; m.p. 118-120°C, yield > 80%.

#### 7.4.3. N-Phthaloylglycine

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

## Materials

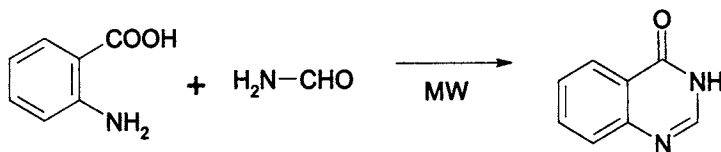
Phthalic anhydride	1.35 g, 9.2 mmol	harmful if swallowed or inhaled, skin or eye contact may cause severe irritation
Glycine	0.69 g, 9.2 mmol	may cause irritation
Xylene	2 ml	eye, skin and respiratory irritant, may act as a narcotic

## Method [100]

1. To a clean reaction vessel add phthalic anhydride (1.35 g, 9.2 mmol), glycine (0.68 g, 9.2 mmol), and xylene (2 ml).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 50% power of the reactor for 10 min. to reach temperature ca. 135°C during the irradiation.
5. Allow the reaction mixture to cool to room temperature and recrystallize the crude product from the mixture of ethyl acetate and hexane; m.p. 194-197°C, yield > 70%.

### 7.4.4. 3H-Quinazolin-4-one

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



## Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

## Materials

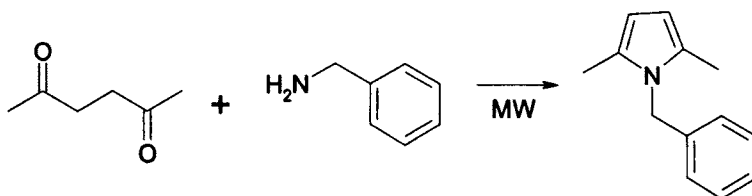
Anthranilic acid	1.37 g, 10 mmol	eye irritant
Formamide	0.45 g, 10 mmol	may
		cause severe burns and blistering
		which may not be immediately
		evident or painful, teratogen

## Method [101]

1. To a clean reaction vessel add anthranilic acid (1.37 g, 10 mmol), and formamide (0.45 g, 10 mmol).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 50% power of the reactor for 20 min. to reach temperature ca. 150°C during the irradiation.
5. Allow the reaction mixture to cool to room temperature, rinse the reaction mixture with ethyl acetate and remove the solvent by rotary evaporation.
6. Purify the product by recrystallization from ethanol; m.p. 214-216°C, yield > 75%.

### 7.4.5. 1-Benzyl-2,5-dimethyl-1H-pyrrole

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



## Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

## Materials

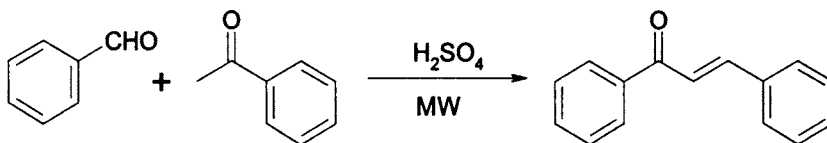
Benzylamine	1.07 g, 10 mmol	harmful if swallowed or inhaled, eye contact may lead to permanent damage
Hexane-2,5-dione (acetylacetone)	1.14 g, 10 mmol	harmful by ingestion, inhalation and through skin contact, may cause neurotoxic effects and permanent eye damage if splashed into eyes

## Method [102]

1. To a clean reaction vessel add benzylamine (1.07 g, 10 mmol), and acetylacetone (1.14 g, 10 mmol).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 8 min. to reach temperature ca. 140°C during the irradiation.
5. Allow the reaction mixture to cool to room temperature, dilute with diethyl ether (5 ml), dry the solution with magnesium sulfate, filter and remove the solvent by rotary evaporation.
6. Purify the product by column chromatography (diethyl ether/hexane 1:5, silica gel); m.p. 37-38°C, yield > 75%.

### 7.4.6. (E)-1,3-Diphenyl-propenone (chalcone)

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



## Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

## Materials

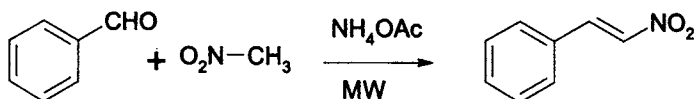
Benzaldehyde	2.80 g, 25 mmol	eye irritant, harmful by inhalation or ingestion, may be harmful by skin contact and cause allergic reaction
Acetophenone	3.00 g, 25 mmol	harmful if swallowed, skin irritant, causes severe eye irritation, may act as a narcotic
Sulphuric acid	0.25 g, 2.5 mmol	highly toxic, ingestion may be fatal, skin contact can lead to severe burns, chronic exposure may result in lung damage and possibly cancer

## Method [85]

1. To a clean reaction vessel add benzaldehyde (2.8 g, 25 mmol), acetophenone (3.0 g, 25 mmol), sulphuric acid (0.25 g, 2.5 mmol).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 10 min. to reach temperature ca. 160°C during the irradiation.
5. Purify the crude product by recrystallization from methanol; m.p. 37-99°C, yield > 75%.

### 7.4.7. $\beta$ -Nitrostyrene

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



## Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

## Materials

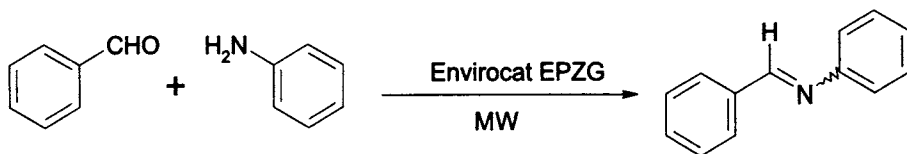
Benzaldehyde	1.06 g, 10 mmol	eye irritant, harmful by inhalation or ingestion, may be harmful by skin contact and cause allergic reaction
Nitromethane	0.61 g, 10 mmol	harmful if swallowed, inhaled or absorbed through skin, irritant, may cause cyanosis
Ammonium acetate	0.19 g, 2.5 mmol	may be harmful by inhalation or ingestion, irritant

## Method [103]

1. To a clean reaction vessel add benzaldehyde (1.1 g, 10 mmol), acetophenone (0.61 g, 10 mmol), and ammonium acetate (0.19 g, 2.5 mmol).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 50% power of the reactor for 20 min. to reach temperature ca. 120°C during the irradiation.
5. Pass the reaction mixture through a short silica gel column (hexane/ethyl acetate 9:1) to afford the product after evaporation of the solvent on a rotary evaporator; m.p. 55-58°C, yield > 760%.

### 7.4.8. Phenyl-[1-phenyl-methylidene]amine

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.





**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

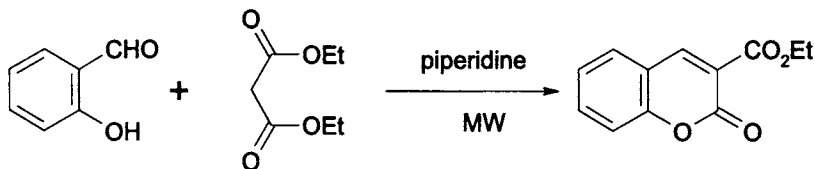
Benzaldehyde	0.53 g, 5.0 mmol	eye irritant, harmful by inhalation or ingestion, may be harmful by skin contact and cause allergic reaction
Aniline	0.47 g, 5.0 mmol	toxic, possible carcinogen, mutagen, and sensitizer, cyanotic reagent, readily absorbed through the skin
Envirocat EPZG	0.10 g	

**Method [104]**

1. To a clean reaction vessel add benzaldehyde (0.53 g, 5.0 mmol), aniline (0.61 g, 10 mmol), and Envirocat EPZG (0.10 g), which is dried by distillation with toluene prior to the reaction.
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 40% power of the reactor for 5 min. to reach temperature ca. 145°C during the irradiation.
5. Extract the product into dichloromethane (10 ml), remove Envirocat EPZG by filtration and wash it with dichloromethane (3 x 10 ml).
6. Remove the solvent by a rotary evaporation to afford the product; m.p. 5–52°C, yield > 80%.

## 7.4.9. 2-Oxo-2H-chromene-3-carboxylic acid ethyl ester

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

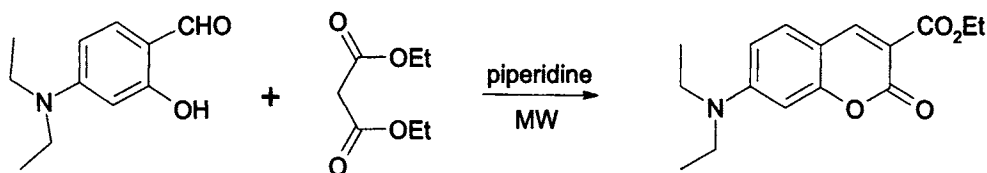
2-Hydroxy-benzaldehyde (Salicylaldehyde)	2.45 g, 20 mmol	harmful if swallowed, inhaled or absorbed through skin, irritant harmful if swallowed poison, may be fatal if inhaled or swallowed, severe irritant, contact with the eyes may lead to permanent damage
Diethyl malonate	3.7 g, 23 mmol	
Piperidine	0.20 g, 2 mmol	

**Method [105]**

1. To a clean reaction vessel add salicylaldehyde (2.45 g, 20 mmol), ethyl malonate (3.7 g, 23 mmol), and piperidine (0.20 g).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 15 min. to reach temperature ca. 140°C during the irradiation.
5. Recrystallize the crude product from ethanol; m.p. 91-92°C, yield > 70%.

**7.4.10. 7-Diethylamino-2-oxo-2H-chromene-3-carboxylic acid ethyl ester**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

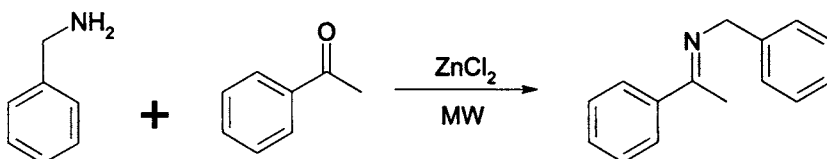
4-(Diethylamino)-salicylaldehyde	3.9 g, 20 mmol	causes eye and skin irritation, may cause digestive tract irritation, causes respiratory tract irritation
Diethyl malonate	3.7 g, 23 mmol	harmful if swallowed
Piperidine	0.20 g, 2 mmol	poison, may be fatal if inhaled or swallowed, severe irritant, contact with the eyes may lead to permanent damage

**Method [105]**

1. To a clean reaction vessel add 4-(diethylamino)salicylaldehyde (3.9 g, 20 mmol), ethyl malonate (3.7 g, 23 mmol), and piperidine (0.20 g).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 10-15 min. to reach temperature ca. 180°C during the irradiation.
5. Recrystallize the crude product from ethanol; m.p. 77-78°C, yield > 50%.

**7.4.11. Benzyl-[1-phenyl-ethylidene]-amine**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

Acetophenone	1.20 g, 10 mmol	harmful if swallowed, skin irritant, causes severe eye irritation, may act as a narcotic
Benzylamine	0.68 g, 9.2 mmol	harmful if swallowed or inhaled, eye contact may lead to permanent damage
Zinc (II) chloride	0.14 g, 1.0 mmol	causes burns, harmful if swallowed or inhaled and in contact with skin, irritant

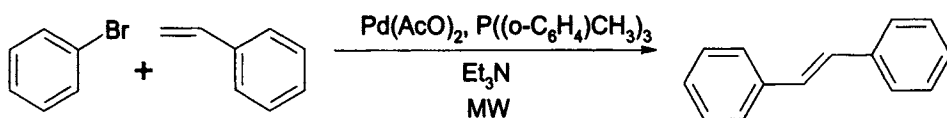
**Method [106]**

1. To a clean reaction vessel add acetophenone (1.2 g, 10 mmol), benzylamine (0.68 g, 9.2 mmol), and zinc (II) chloride (0.14 g, 1.0 mmol).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 30% power of the reactor for 60 min. to reach temperature ca. 140°C during the irradiation.

5. Allow the reaction mixture to cool to room temperature, dilute with diethyl ether, dry the solution with magnesium sulfate, filter and remove the solvent by rotary evaporation.
6. Purify the product by Kugelrohr distillation; b.p. 162°C /10 mmHg, yield > 60%.

#### 7.4.12. *trans*-1,2-Diphenylethylene (*trans*-stilbene)

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

#### Materials

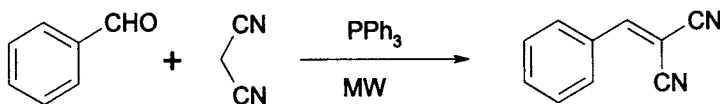
Styrene	0.18 g, 1.75 mmol	toxic, carcinogen, mutagen, lachrymator, harmful by inhalation, ingestion and through skin absorption
Bromobenzene	0.22 g, 1.40 mmol	harmful if inhaled, may be harmful if swallowed or absorbed through the skin, severe irritant
Palladium acetate (II)	3.1 mg, 1.4 10 <sup>-5</sup> mmol	avoid contact with skin and eyes
Triethylamine	0.70 ml, 5.0 mmol	extremely flammable, harmful by ingestion, inhalation and if absorbed through the skin, chronic exposure may cause liver damage, lachrymator
Tri- <i>o</i> -tolylphosphine	8.4 mg, 0.027 mmol	irritating to eyes, respiratory system and skin

**Method [107]**

1. To a clean reaction vessel add styrene (0.18 g, 1.75 mmol), bromobenzene (0.22 g, 1.40 mmol), palladium acetate (II) (3.1 mg, 1.4  $10^{-5}$  mmol), triethylamine (0.70 ml, 5.0 mmol), tri-*o*-tolylphosphine (8.4 mg, 0.027 mmol).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 30% power of the reactor for 10 min. to reach temperature ca. 130°C during the irradiation. Since some fumes can be generated during the process, stop the reaction as soon as they appear.
5. Allow the reaction mixture to cool to room temperature, dilute with dichloromethane (2 x 20 ml), and wash the extract with a diluted hydrochloric acid (5% aq. solution) (2 x 20 ml).
6. Dry the solution with magnesium sulfate, filter and remove the solvent by rotary evaporation.
7. Purify the product by flash chromatography; b.p. 123-125°C, yield > 75%.

**7.4.13. 2-Benzylidene-malononitrile**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

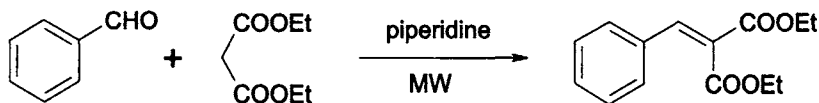
Benzaldehyde	1.37 g, 13 mmol	eye irritant, harmful by inhalation or ingestion, may be harmful by skin contact and cause allergic reaction
Malononitrile	0.66 g, 10 mmol	toxic by inhalation, in contact with skin and if swallowed
Triphenylphosphine	0.61 g, 2.0 mmol	harmful if swallowed or inhaled. causes irritation to skin, eyes and respiratory tract

**Method [108]**

1. To a clean reaction vessel add benzaldehyde (1.37 g, 13 mmol), malononitrile (0.66 g, 10 mmol), and triphenylphosphine (0.61 g, 2.0 mmol).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 30% power of the reactor for 10 min. to reach temperature ca. 130°C during the irradiation and then for another 10 min. to reach the final temperature ca. 100°C .
5. Allow the reaction mixture to cool to room temperature and purify the crude product by recrystallization from ethanol; m.p. 83-85°C , yield > 65%.

**7.4.14. Diethyl benzylidenemalonate**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

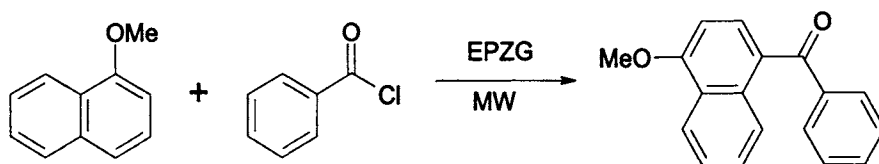
Benzaldehyde	1.06 g, 10 mmol	eye irritant, harmful by inhalation or ingestion, may be harmful by skin contact and cause allergic reaction
Diethyl malonate	1.6 g, 10 mmol	harmful if swallowed
Piperidine	0.10 g, 1.0 mmol	poison, may be fatal if inhaled or swallowed, severe irritant, contact with the eyes may lead to permanent damage

**Method [109]**

1. To a clean reaction vessel add benzaldehyde (1.1 g, 10 mmol), diethyl malonate (1.6 g, 10 mmol), and piperidine (0.10 g, 1.0 mmol).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 20 min. to reach temperature ca. 150°C during the irradiation.
5. Allow the reaction mixture to cool to room temperature and purify the crude product by Kugelrohr distillation; b.p. 215–217°C /30 mmHg, yield > 65%.

**7.4.15. (4-Methoxy-naphthalen-1-yl)-phenyl-methanone**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger



**Materials**

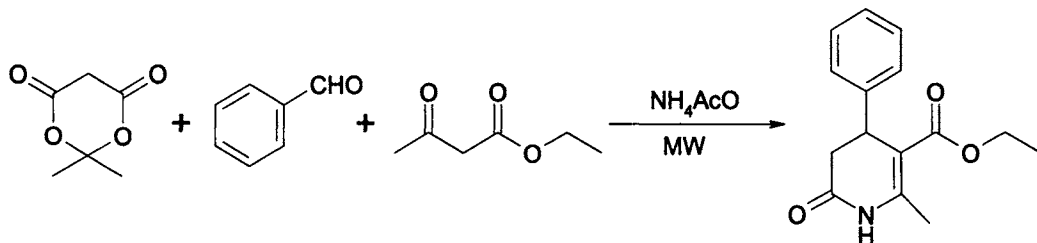
1-Methoxynaphthalene	3.16 g, 20 mmol	avoid contact with skin and eyes
Benzoyl chloride	2.8 g, 20 mmol	poison, may be fatal if inhaled, possible carcinogen, harmful if swallowed, corrosive - causes severe burns, vapour is very irritating.
Envirocat EPZG	0.50 g	

**Method [110]**

1. To a clean reaction vessel add 1-methoxynaphthalene (3.16 g, 20 mmol), benzoyl chloride (2.8 g, 20 mmol), and Envirocat EPZG (0.50 g), which is dried by distillation with toluene prior to the reaction.
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 5 min. to reach temperature ca. 180°C during the irradiation.
5. Allow the reaction mixture to cool to room temperature, dilute with dichloromethane (50 ml), and filter off.
6. Wash the extract with a saturated sodium bicarbonate (2 x 20 ml), dry the solution with sodium sulfate, filter and remove the solvent by rotary evaporation.
7. Purify the product by column chromatography (ethyl acetate/hexane 1:7, silica gel); m.p. 84-86°C, yield > 60%.

#### 7.4.16. 2-Methyl-6-oxo-4-phenyl-1,4,5,6-tetrahydro-pyridine-3-carboxylic acid ethyl ester

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

#### Materials

2,2-Dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid)	0.58 g, 4.0 mmol	may cause eye, skin, and respiratory tract irritation
Benzaldehyde	0.42 g, 4.0 mmol	eye irritant, harmful by inhalation or ingestion, may be harmful by skin contact and cause allergic reaction
Methyl acetoacetate	0.48 g, 4.0 mmol	severe eye irritant, mucous membrane and respiratory irritant, may be harmful by inhalation
Ammonium acetate	0.31 g, 4.0 mmol	may be harmful by inhalation or ingestion, irritant

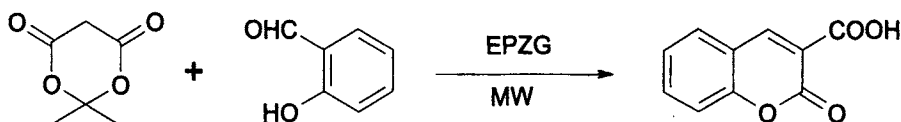
#### Method [111]

1. To a clean reaction vessel add Meldrum's acid (0.58 g, 4.0 mmol), benzaldehyde (0.42 g, 4.0 mmol), methyl acetoacetate (0.48 g, 4.0 mmol), and ammonium acetate (0.31 g, 4.0 mmol).

2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 30% power of the reactor for 10 min. to reach temperature ca. 120°C during the irradiation.
5. Allow the reaction mixture to cool to room temperature purify the crude product by recrystallization from ethanol; m.p. 196-198°C , yield > 70%.

#### 7.4.17. 2-Oxo-2H-chromene-3-carboxylic acid

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

#### Materials

2-Hydroxy-benzaldehyde (Salicylaldehyde)	0.61 g, 5.0 mmol	<b>harmful if swallowed, inhaled or absorbed through skin, irritant may cause eye, skin, and respiratory tract irritation</b>
2,2-Dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid)	0.72 g, 5.0 mmol	
Envirocat EPZG	0.10 g	

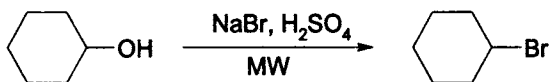
#### Method [112]

1. To a clean reaction vessel add Meldrum's (0.72 g, 5.0 mmol), salicylaldehyde (0.61 g, 5.0 mmol), and Envirocat EPZG (0.10 g), which is dried by distillation with toluene prior to the reaction.

2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 10 min. to reach temperature ca. 160°C during the irradiation.
5. Allow the reaction mixture to cool to room temperature, dilute with diethyl ether (50 ml), filter and remove the solvent by rotary evaporation.
6. Purify the product by recrystallization from ethanol; m.p. 189-191°C, yield > 60%.

#### 7.4.18. Bromocyclohexane

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

#### Materials

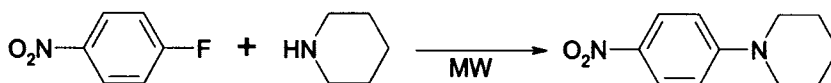
Cyclohexanol	1.0 g, 10 mmol	harmful by inhalation, ingestion or skin absorption, severe skin and eye irritant
Sodium bromide	1.0 g, 10 mmol	skin, eye and respiratory irritant, prolonged exposure may lead to bromide rashes
Sulphuric acid	2 ml	highly toxic, ingestion may be fatal, skin contact can lead to severe burns, chronic exposure may result in lung damage and possibly cancer

**Method [50]**

1. To a clean reaction vessel add cyclohexanol (1.0 g, 10 mmol), sodium bromide (1.0 g, 10 mmol), and sulphuric acid (2 ml).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 30% power of the reactor for 10 min. to reach temperature ca. 130°C during the irradiation.
5. Allow the reaction mixture to cool to room temperature and the reaction mixture into water (2 ml).
6. Extract the reaction mixture with ethyl acetate (2 x 20 ml), dry the organic phase with magnesium sulfate, filter and remove the solvent by rotary evaporation.
7. Purify the product by Kugelrohr distillation; b.p. 166-167°C, yield > 50%.

**7.4.19. 1-(4-Nitro-phenyl)-piperidine**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

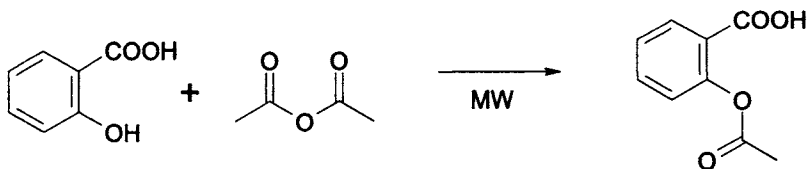
4-Fluoronitrobenzene	1.41 g g, 10 mmol	harmful by ingestion, inhalation and through skin contact, readily absorbed through the skin, may cause irritation
Piperidine	0.85 g, 10 mmol	poison, may be fatal if inhaled or swallowed, severe irritant, contact with the eyes may lead to permanent damage

**Method [113]**

1. To a clean reaction vessel add 4-fluoronitrobenzene (1.41 g, 10 mmol), and piperidine (0.85 g, 10 mmol).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 50% power of the reactor for 10 min. to reach temperature ca. 120°C during the irradiation.
5. Allow the reaction mixture to cool to room temperature, and charge directly on the top chromatography column (silica gel).
6. Purify the product by column chromatography (hexane/ethyl acetate 7:3); m.p. 102-104°C, yield > 60%.

**7.4.20. 2-Acetoxy-benzoic acid (aspirine)**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

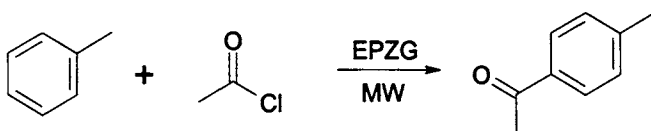
2-Hydroxy-benzoic acid (Salicylic acid)	3.45 g, 24 mmol	<b>harmful by inhalation, ingestion and through skin absorption, irritant, laboratory experiments have shown mutagenic effects</b> <b>posion, Corrosive. Causes severe burns. Harmful if swallowed or inhaled. Causes severe respiratory irritation. Eye contact may cause serious irritation or burns.</b>
Acetic anhydride	3.7 g, 23 mmol	

**Method**

1. To a clean reaction vessel add salicylic acid (3.45 g, 24 mmol), and acetic anhydride (3.7 g, 23 mmol).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 10 min. to reach temperature ca. 130-140°C during the irradiation.
5. Allow the reaction mixture to cool to 95-100°C and pour it into cold water. The mixture should be stirred until the solid stars separating out.
6. Keep the mixture when cold and cool in a bath of ice cold water. Filter the mixture and wash the product with ice water then dry under vacuum suction.
7. If necessary, recrystallize the product from a hot mixtue of propanol and water (7:2); m.p. 136-138°C , yield > 70%.

**7.4.21. 4-Methylacetophenone**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

Toluene	0.46 g, 5.0 mmol	<b>highly flammable, toxic by inhalation, ingestion or by absorption through skin, serious irritant, experimental teratogen corrosive - causes severe burns, harmful if inhaled or swallowed, and in contact with skin, contact with water generates phosgene - very toxic! may cause permanent eye damage if splashed in the eyes</b>
Acetyl chloride	0.55 g, 7.0 mmol	
Envirocat EPZG	100 mg	

**Method [114]**

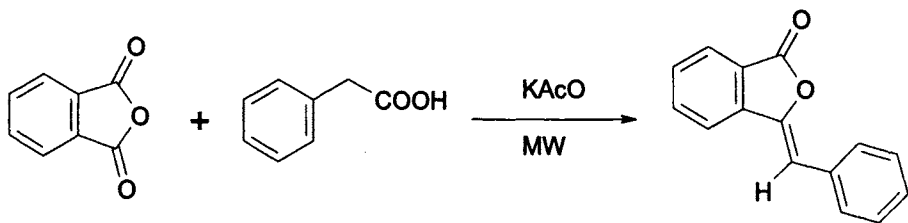
1. To a clean reaction vessel add toluene (0.46 g, 5.0 mmol), acetyl chloride (0.55 g, 7.0 mmol), and Envirocat EPZG (100 mg).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).



4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 5 min. to reach temperature ca. 55°C during the irradiation then 40% power for 5 min. to reach the final temperature ca. 80°C.
5. Allow the reaction mixture to cool to room temperature, filter off the catalyst, and rinse it with dichloromethane (2 x 10 ml).
6. Remove the solvent by rotary evaporation; if necessary, purify the product by column chromatography; m.p. 22-24°C ; yield > 70%.

#### 7.4.22. 3-[1-Phenyl-methylidene]-3H-isobenzofuran-1-one

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses. Never use flat-bottomed flask with rotary evaporators.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

#### Materials

Phthalic anhydride      1.48 g, 10 mmol

Phenylacetic acid      1.36 g, 10 mmol

Potassium acetate      0.198 g, 2.0 mmol

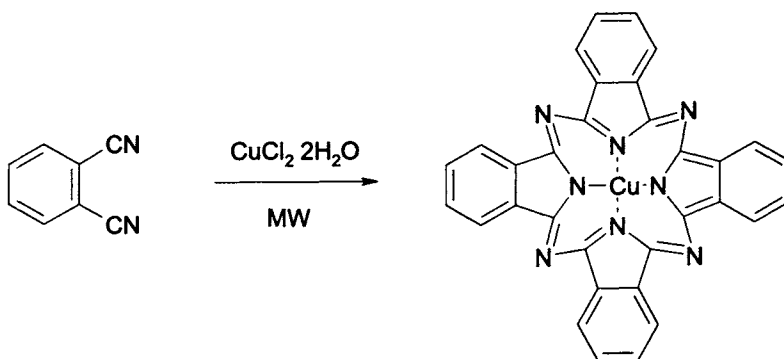
harmful if swallowed or inhaled, skin or eye contact may cause severe irritation  
harmful by ingestion, inhalation or through skin contact, severe eye irritant, skin and respiratory irritant, may act as a teratogen  
may cause mild irritation to the respiratory tract, may cause mild skin irritation and redness

**Method [115]**

1. To a clean reaction vessel add phthalic anhydride (1.48 g, 10 mmol), phenylacetic acid (1.36 g, 10 mmol), and potassium acetate (0.198 g, 2.0 mmol).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture with 20% power of the reactor for 10 min. to reach temperature ca. 165°C during the irradiation.
5. Allow the reaction mixture to cool to room temperature, pour it into a solution of sodium bicarbonate (5% aq. solution) (100 ml) and leave to stand overnight.
6. Filter off the precipitated solid and recrystallize the product from ethanol; m.p. 99-102°C ; yield > 70%.

**7.4.23. Phthalocyanine**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

1,2-dicyanobenzene    1.54 g, 12 mmol

**toxic, toxic by inhalation, in  
contact with skin and if  
swallowed**

Cupric (II) chloride 0.42 g, 2.5 mmol

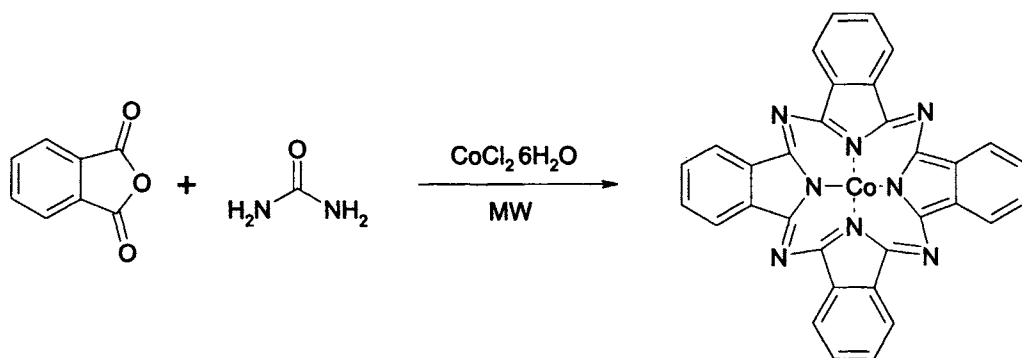
**harmful if swallowed or inhaled,  
severe eye irritant, skin and  
respiratory irritant, long-term  
contact may lead to systemic  
copper poisoning**

#### Method [116]

1. Ground together a mixture of phthalodinitrile (1.54 g, 12 mmol) and copper chloride (0.425 g, 2.5 mmol) and put it to a clean reaction vessel.
2. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
3. Rotating the reaction vessel (if possible), irradiate the mixture with stirring with full power of the reactor so that temperature rises to ca. 190-210°C and maintain temperature for another 10 min.
4. Wash the solid successively with hot water, acetone, dichloromethane and then dry.
5. Dissolve the product with concentrated sulphuric acid, precipitate it from water, filter off, wash to neutral pH, and dry under vacuum; yield > 80%.

#### 7.4.24. Phthalocyanine

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

Cold finger

**Materials**

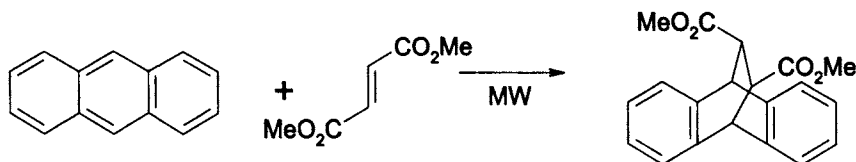
Phthalic anhydride	1.49 g, 10 mmol	harmful if swallowed or inhaled, skin or eye contact may cause severe irritation
Urea	1.2 g, 20 mmol	irritant, prolonged exposure may cause allergic reaction in some individuals
Cupric (II) chloride	0.42 g, 2.5 mmol	harmful if swallowed or inhaled, severe eye irritant, skin and respiratory irritant, long-term contact may lead to systemic copper poisoning
Ammonium molybdate	0.47 g, 2.0 mmol	possible mutagen, possible risk of irreversible effects, harmful by inhalation, ingestion or skin absorption, irritant

**Method [116]**

1. Ground together a mixture of phthalic anhydride (10 mmol, 1.54 g) and copper chloride (2.5 mmol, 0.425 g) and put it to a clean reaction vessel together with urea (1.2 g, 20 mmol), and ammonium molybdate (0.47 g, 2.0 mmol).
2. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
3. Rotating the reaction vessel (if possible), irradiate the mixture with stirring with full power of the reactor so that temperature rises to ca. 200°C . and maintain temperature for another 10 min.
4. Wash the solid successively with hot water, acetone, dichloromethane and then dry.
5. Dissolve the product with concentrated sulphuric acid, precipitate it from water, filter off, wash to neutral pH, and dry under vacuum; yield > 80%.

**7.4.25. trans-9,10-Dihydro-9,10-ethanoanthracene dicarboxylic acid dimethyl ester**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (Figure 4.2a)

Adapter (Figure 4.2f)

Cold finger

**Materials**

Anthracene                      1.78 g, 10 mmol

Dimethyl fumarate          1.72 g, 10 mmol

harmful by inhalation or  
ingestion, may be harmful in  
contact with skin, suspected  
carcinogen  
skin irritant, severe eye irritant -  
eye contact may lead to serious  
damage, may act as a sensitizer

**Method [17]**

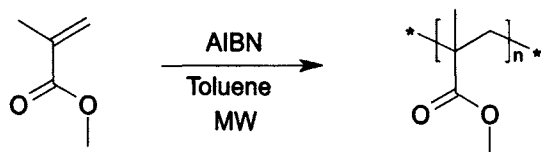
1. To a clean reaction vessel add anthracene (1.78 g, 10 mmol), and dimethyl fumarate (1.72 g, 10 mmol).
2. Stir the mixture for 20 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel, place it in the microwave reactor, and put the cold finger (Figure 4.4a).
4. Rotating the reaction vessel (if possible), irradiate the mixture starting with 70% power of the reactor so that temperature rises to ca. 220-230°C . and maintain temperature for another 15 min.

5. Allow the reaction mixture to cool to room temperature, dissolve the solid in DMF and leave to stand overnight.
6. Filter off the product and dry under vacuum. If necessary, recrystallize the product from ethanol; m.p. 160-162°C , yield > 60%.

## 7.5. Polymerization reactions

### 7.5.1. Poly(methyl methacrylate)

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (10 ml borosilicate tube)

### Materials

Methyl methacrylate	1 ml, 10 mmol	flammable, may react violently with polymerization initiators, harmful if swallowed, inhaled or absorbed through the skin, lachrymator, corrosive, may act as a sensitizer
2,2'-Azobis(2-methylpropionitrile) (AIBN)	0.010 g, 0.060 mmol	flammable solid, shock sensitive, thermally unstable, may be fatal if swallowed, may cause degenerative brain changes, may cause liver or kidney damage, respiratory irritant
Toluene	1 ml	highly flammable, toxic by inhalation, ingestion or by absorption through skin, serious irritant, experimental teratogen

### Method [117]

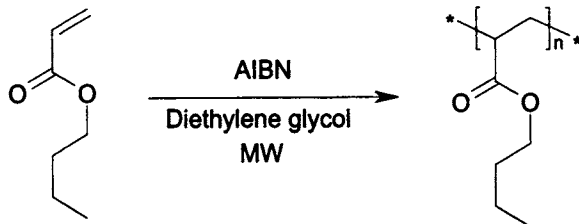
*Note:* Methyl methacrylate should be purified to remove inhibitors prior to use.

1. Dry carefully the reaction vessel and purge it with dry argon or nitrogen.

2. Place methyl methacrylate (1 ml, 10 mmol) in the reaction vessel together with anhydrous toluene (1 ml).
3. Add AIBN (0.010 g, 0.060 mmol) and shake the vessel firmly for a few seconds.
4. Purge the solution with dry argon or nitrogen and seal the vessel with an appropriate rubber septum.
5. Carry out the freeze-thaw-degassing procedure in the same time vacuum and purge the vessel with dry argon or nitrogen to ensure all oxygen is removed from the system.
6. Place the vessel in the cavity of the single-mode microwave reactor and heat the solution up to 90°C for 10 min.
7. Remove the vessel from the reactor and allow to cool to room temperature.
8. Precipitate the resultant polymer into an ethanol solution (30 ml) and filter it through a filter paper.
9. Transfer the solid obtained to a large watch glass and dry it in air. Once a consistent weight is achieved, record the crude yield. Yields > 50% are typical.
10. Analyse the product using gel permeation chromatography (GPC) to determine  $M_n$  and  $M_w$ . ( $M_n = 1.810^4$ ,  $M_w = 2.610^4$ )

### 7.5.2. Poly(butyl acrylate)

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (10 ml borosilcate tube)



**Materials**

Butyl acrylate	1.0 ml, 7.0 mmol	flammable, harmful if swallowed or inhaled, and in contact with the skin, lachrymator, limited evidence of carcinogenic effect
2,2'-Azobis(2-methylpropionitrile) (AIBN)	0.010 g, 0.060 mmol	flammable solid, shock sensitive, thermally unstable, may be fatal if swallowed, may cause degenerative brain changes, may cause liver or kidney damage, respiratory irritant
Diethylene glycol	1 ml	may be harmful or act as an irritant - toxicology not fully investigated

**Method [117]**

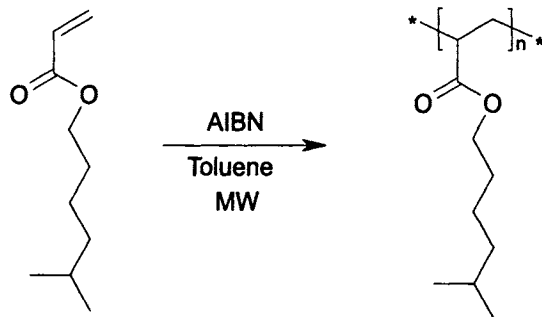
*Note:* Butyl acrylate should be purified to remove inhibitors prior to use.

1. Dry carefully the reaction vessel and purge it with dry argon or nitrogen.
2. Place butyl acrylate (1 ml, 7.0 mmol) in the reaction vessel together with anhydrous diethylene glycol (1 ml).
3. Add AIBN (0.010 g, 0.060 mmol) and shake the vessel firmly for a few seconds.
4. Purge the solution with dry argon or nitrogen and seal the vessel with an appropriate rubber septum.
5. Carry out the freeze-thaw-degassing procedure in the same time vacuum and purge the vessel with dry argon or nitrogen to ensure all oxygen is removed from the system.
6. Place the vessel in the cavity of the single-mode microwave reactor and heat the solution up to 65°C for 10 min.
7. Remove the vessel from the reactor and allow to cool to room temperature.
8. Precipitate the resultant polymer into an ethanol solution (30 ml) and filter it through a filter paper.
9. Transfer the solid obtained to a large watch glass and dry it at air. Once a consistent weight is achieved, record the crude yield. Yields > 60% are typical.

10. Analyse the product using gel permeation chromatography (GPC) to determine  $M_n$  and  $M_w$ . ( $M_n = 1.310^5$ ,  $M_w = 2.110^4$ )

### 7.5.3. Poly(isooctyl acrylate)

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (10 ml borosilcate tube)

### Materials

Isooctyl acrylate	1.0 ml, 5.0 mmol	<b>repeated exposure may cause an allergic skin reaction flammable solid, shock sensitive, thermally unstable, may be fatal if swallowed, may cause degenerative brain changes, may cause liver or kidney damage, respiratory irritant</b>
2,2'-Azobis(2-methylpropionitrile) (AIBN)	0.010 g, 0.060 mmol	
Hexane	1 ml	
		<b>highly flammable, harmful by inhalation, ingestion or skin absorption, prolonged exposure may cause serious health damage</b>

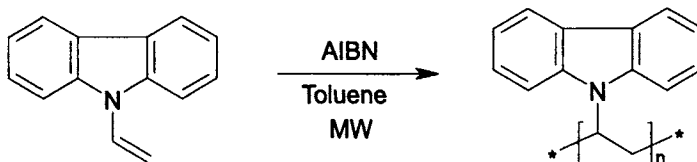
### Method [117]

*Note:* Isooctyl acrylate should be purified to remove inhibitors prior to use.

1. Dry carefully the reaction vessel and purge it with dry argon or nitrogen.
2. Place isooctyl acrylate (1 ml, 5.0 mmol) in the reaction vessel together with anhydrous hexane (1 ml).
3. Add AIBN (0.010 g, 0.060 mmol) and shake the vessel firmly for a few seconds.
4. Purge the solution with dry argon or nitrogen and seal the vessel with an appropriate rubber septum.
5. Carry out the freeze-thaw-degassing procedure in the same time vacuum and purge the vessel with dry argon or nitrogen to ensure all oxygen is removed from the system.
6. Place the vessel in the cavity of the single-mode microwave reactor and heat the solution up to 65°C for 10 min.
7. Remove the vessel from the reactor and allow to cool to room temperature.
8. Precipitate the resultant polymer into an ethanol solution (30 ml) and filter it through a filter paper.
9. Transfer the solid obtained to a large watch glass and dry it at air. Once a consistent weight is achieved, record the crude yield. Yields > 60% are typical.
10. Analyse the product using gel permeation chromatography (GPC) to determine  $M_n$  and  $M_w$ . ( $M_n = 3.610^4$ ,  $M_w = 1.110^5$ )

#### 7.5.4. Poly(9-vinylcarbazole)

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



#### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (10 ml borosilcate tube)

**Materials**

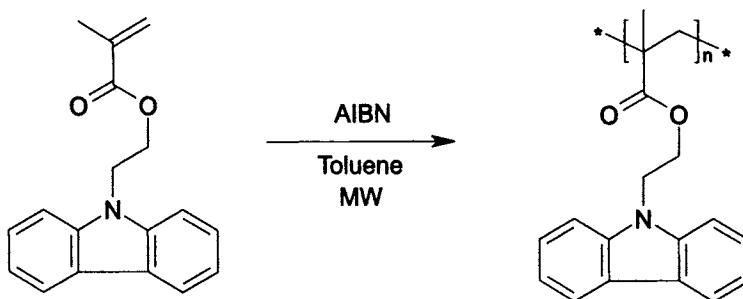
9-Vinylcarbazole	1.0 ml, 10 mmol	harmful if swallowed or absorbed through the skin
2,2'-Azobis(2-methylpropionitrile) (AIBN)	0.010 g, 0.060 mmol	flammable solid, shock sensitive, thermally unstable, may be fatal if swallowed, may cause degenerative brain changes, may cause liver or kidney damage, respiratory irritant
Toluene	1 ml	highly flammable, toxic by inhalation, ingestion or by absorption through skin, serious irritant, experimental teratogen

**Method [117]**

1. Dry carefully the reaction vessel and purge it with dry argon or nitrogen.
2. Place 9-vinylcarbazole (1.0 g, 5.0 mmol) in the reaction vessel together with anhydrous toluene (1 ml).
3. Add AIBN (0.010 g, 0.060 mmol) and shake the vessel firmly for a few seconds.
4. Purge the solution with dry argon or nitrogen and seal the vessel with an appropriate rubber septum.
5. Carry out the freeze-thaw-degassing procedure in the same time vacuum and purge the vessel with dry argon or nitrogen to ensure all oxygen is removed from the system.
6. Place the vessel in the cavity of the single-mode microwave reactor and heat the solution up to 65°C for 10 min.
7. Remove the vessel from the reactor and allow to cool to room temperature.
8. Precipitate the resultant polymer into an ethanol solution (30 ml) and filter it through a filter paper.
9. Transfer the solid obtained to a large watch glass and dry it in air. Once a consistent weight is achieved, record the crude yield. Yields > 75% are typical.
10. Analyse the product using gel permeation chromatography (GPC) to determine  $M_n$  and  $M_w$ . ( $M_n = 1.610^4$ ,  $M_w = 7.310^4$ )

## 7.5.5. Poly(2-(9-carbazolyethyl methacrylate)

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (10 ml borosilicate tube)

**Materials**

2-Carbazol-9-ylethyl methacrylate	1.0 ml, 10 mmol
2,2'-Azobis(2-methylpropionitrile) (AIBN)	0.010 g, 0.060 mmol

**harmful if swallowed or absorbed through the skin**  
**flammable solid, shock sensitive, thermally unstable, may be fatal if swallowed, may cause degenerative brain changes, may cause liver or kidney damage, respiratory irritant**  
**highly flammable, toxic by inhalation, ingestion or by absorption through skin, serious irritant, experimental teratogen**

Toluene	1 ml
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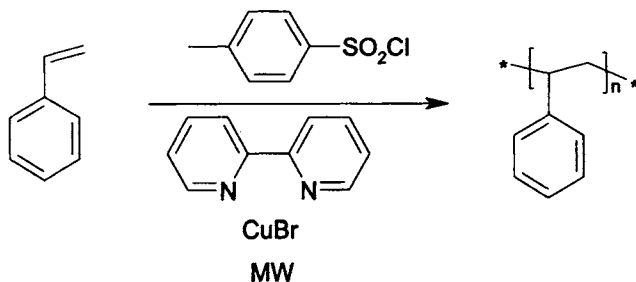
**Method [117]**

1. Dry carefully the reaction vessel and purge it with dry argon or nitrogen.
2. Place 2-Carbazol-9-ylethyl methacrylate (1.0 g, 3.0 mmol) in the reaction vessel together with anhydrous toluene (1 ml).

3. Add AIBN (0.010 g, 0.060 mmol) and shake the vessel firmly for a few seconds.
4. Purge the solution with dry argon or nitrogen and seal the vessel with an appropriate rubber septum.
5. Carry out the freeze-thaw-degassing procedure in the same time vacuum and purge the vessel with dry argon or nitrogen to ensure all oxygen is removed from the system.
6. Place the vessel in the cavity of the single-mode microwave reactor and heat the solution up to 65°C for 10 min.
7. Remove the vessel from the reactor and allow to cool to room temperature.
8. Precipitate the resultant polymer into an ethanol solution (30 ml) and filter it through a filter paper.
9. Transfer the solid obtained to a large watch glass and dry it in air. Once a consistent weight is achieved, record the crude yield. Yields > 75% are typical.
10. Analyse the product using gel permeation chromatography (GPC) to determine  $M_n$  and  $M_w$ . ( $M_n = 2.110^4$ ,  $M_w = 5.110^4$ )

### 7.5.6. Polystyrene

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



### Equipment

Single-mode microwave reactor equipped with a pyrometer (300 W)

Reaction vessel (25 ml borosilicate tube)

**Materials**

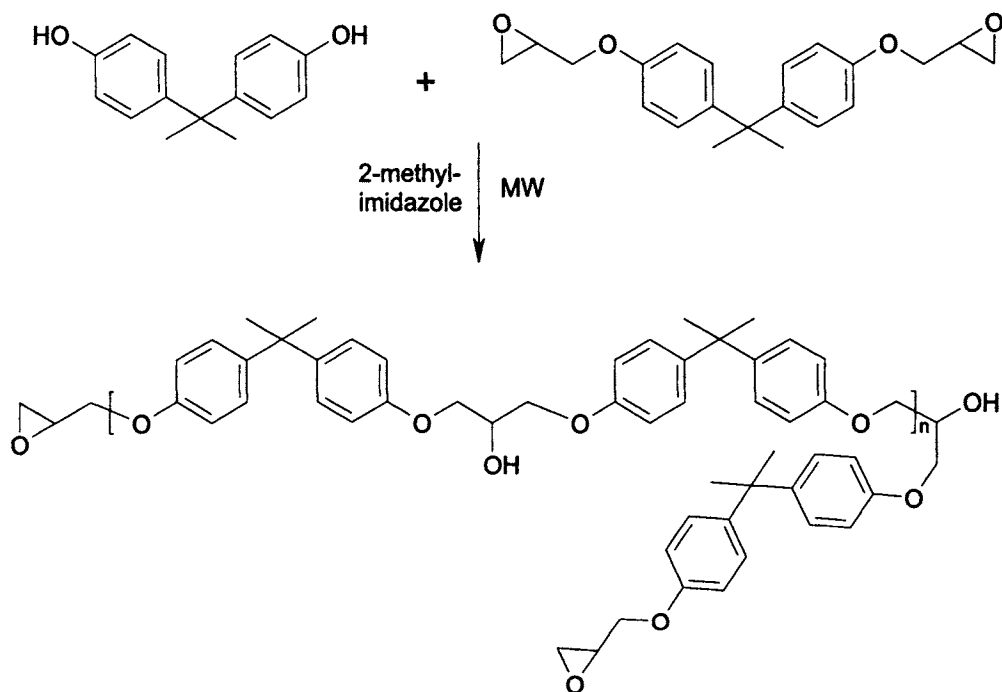
Styrene	6.0 g, 58 mmol	toxic, carcinogen, mutagen, lachrymator, harmful by inhalation, ingestion and through skin absorption
p-Toluenesulfonyl chloride	0.11 g, 0.60 mmol	this material is corrosive and causes burns, it is also a lachrymator, harmful in contact with skin or if swallowed, very destructive of mucous membranes
Cupric bromide (I)	0.088 g, 0.61 mmol	irritant, chronic exposure to copper salts is harmful
2,2-bipyridine	0.20 g, 1.3 mmol	harmful if swallowed, may be harmful if inhaled or absorbed through skin, causes irritation to skin, eyes and respiratory tract

**Method**

1. Dry carefully the reaction vessel and purge it with dry argon or nitrogen.
2. Place p-toluenesulfonyl chloride (0.11 g, 0.60 mmol), cupric bromide (I) (0.088 g, 0.61 mmol), and 2,2-bipyridine (0.20 g, 1.3 mmol) and styrene (6.0 g, 58 mmol).
3. Purge the solution with dry argon or nitrogen and seal the vessel with an appropriate rubber septum.
4. Carry out the freeze-thaw-degassing procedure in the same time vacuum and purge the vessel with dry argon or nitrogen to ensure all oxygen is removed from the system.
5. Place the vessel in the cavity of the single-mode microwave reactor and irradiate the solution up to 110°C for 2 h.
6. Remove the vessel from the reactor, allow to cool to room temperature and dissolve the resultant polymer in the minimum volume of THF.
7. Precipitate the resultant polymer into an cold ethanol solution (50 ml) and filter it through a filter paper.
8. Transfer the solid obtained to a large watch glass and dry it in air. Once a consistent weight is achieved, record the crude yield. Yields > 50% are typical.

**7.5.7. High molecular weight (solid) epoxy resins - bisphenol A**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer(600 W)

Reaction vessel (250 ml round-bottomed flask)

Long-neck adapter (Figure 4.1)

Reflux condenser



**Materials**

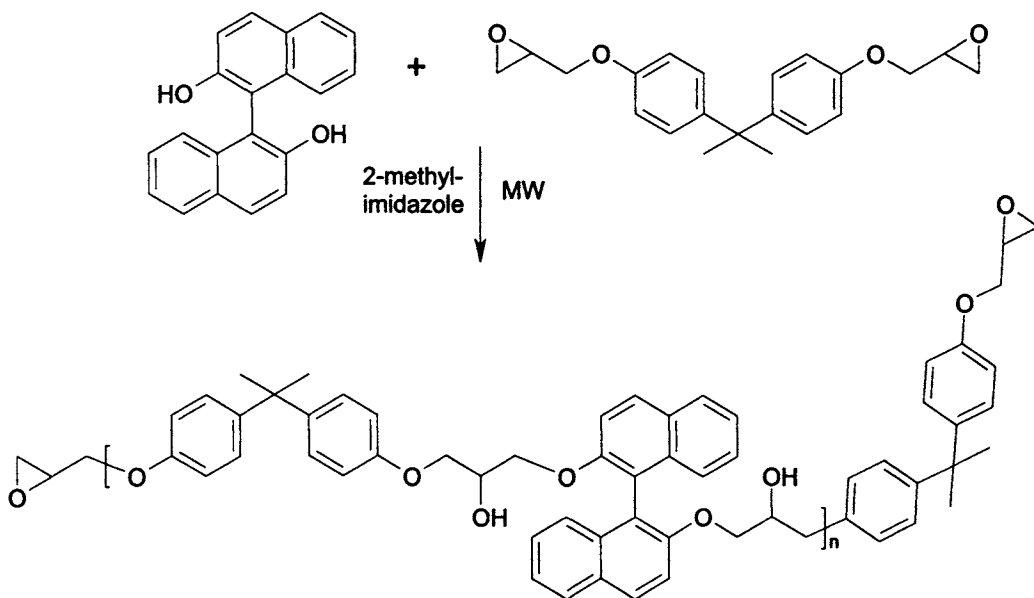
4,4'-Isopropylidenediphenol (Bisphenol A)	11.0 g, 48 mmol	causes severe eye irritation, skin and respiratory irritant, may be harmful - toxicology not fully investigated, experimental teratogen, may affect fertility, may cause sensitization
Diglycidyl ether of bisphenol A (low molecular weight epoxy resins: epoxy value ca. 0.57 mol/100 g)	25 g, 73 mmol	can cause eye and skin irritation
2-Methylimidazole	19 mg, 0.24 mmol	corrosive, causes burns by all exposure routes, harmful if swallowed, inhalation may be fatal as a result of spasm and inflammation

**Method [118]**

1. To a round-bottomed flask (250 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add low molecular weight epoxy resin (25 g, 73 mmol), bisphenol-A (11 g, 48 mmol) and 2-methylimidazole (19 mg, 0.24 mmol).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter and reflux condenser.
3. Irradiate the reaction mixture to 160°C for 40 min. whilst stirring.
4. Remove carefully the hot flask from the microwave reactor and pour the reaction mixture into a large glass Petri dish.
5. Allow the reaction mixture to cool to room temperature and powder it.
6. Analyse the product using gel permeation chromatography (GPC) to determine  $M_n$  and  $M_w$ . ( $M_n = 1850$ ,  $M_w = 3390$ ) and determine epoxy value EV (EV= 0.11 mol/100 g).

**7.5.8. High molecular weight (solid) epoxy resins - 1,1'-Bi-2-naphthol**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer(600 W)

Reaction vessel (250 ml round-bottomed flask)

Long-neck adapter (Figure 4.1)

Reflux condenser

**Materials**

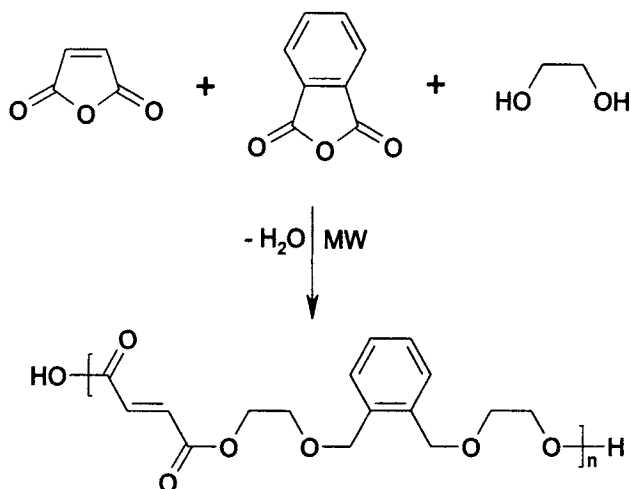
1,1'-Bi-2-naphthol	13.8 g, 48 mmol	<b>irritant, causes respiratory tract irritation, causes eye and skin irritation</b>
Diglycidyl ether of bisphenol A (low molecular weight epoxy resins: epoxy value ca. 0.57 mol/100 g)	25 g, 0.060 mmol	<b>can cause eye and skin irritation</b>
2-Methylimidazole	19 mg, 0.24 mmol	<b>corrosive, causes burns by all exposure routes, harmful if swallowed, inhalation may be fatal as a result of spasm and inflammation</b>

**Method [119]**

1. To a round-bottomed flask (250 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add low molecular weight epoxy resin (25 g, 73 mmol), 1,1'-bi-2-naphthol (13.8 g, 48 mmol) and 2-methylimidazole (19 mg, 0.24 mmol).
2. Place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter and reflux condenser.
3. Irradiate the reaction mixture to 180°C for 30 min. whilst stirring.
4. Remove carefully the hot flask from the microwave reactor and pour the reaction mixture into a large glass Petri dish.
5. Allow the reaction mixture to cool to room temperature and powder it.
6. Analyse the product using gel permeation chromatography (GPC) to determine  $M_n$  and  $M_w$ . ( $M_n = 1090$ ,  $M_w = 2020$ ) and determine epoxy value EV (EV = 0.18 mol/100 g).

## 7.5.9. Unsaturated polyester resin - polycondensation

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer(600 W)

Reaction vessel (250 ml round-bottomed flask)

Long-neck adapter (Figure 4.1)

Reflux condenser

Dean-Stark trap for azeotropic distillation

**Materials**

Maleic anhydride	21 g, 215 mmol	harmful if swallowed, inhaled or absorbed through the skin, corrosive - causes burns, irritant
Phthalic anhydride	42 g, 285 mmol	can cause eye and skin irritation
Ethylene glycol	17 g, 270 mmol	harmful if swallowed, may be harmful if inhaled or in contact with the skin, skin and respiratory irritant, severe eye irritant

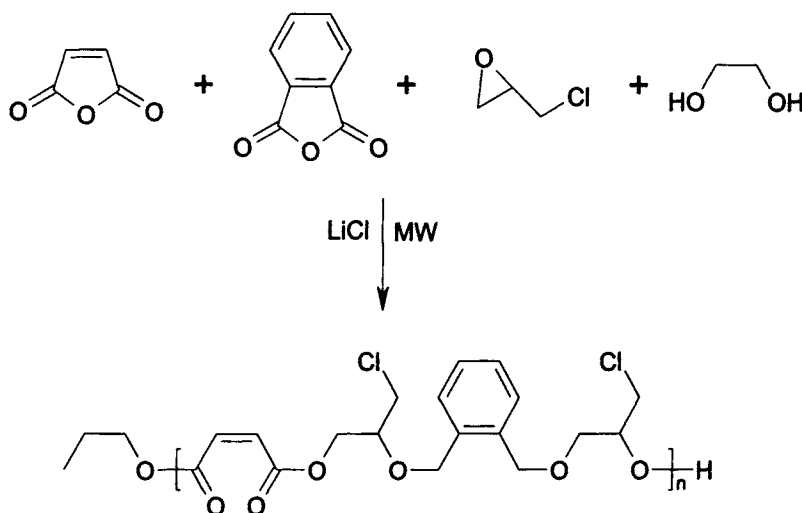
Propylene glycol	20 g, 270 mmol	causes irritation, avoid contact with eyes, skin
Xylene	12 ml	eye, skin and respiratory irritant, may act as a narcotic

**Method [120]**

1. To a round-bottomed flask (250 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add maleic anhydride (21 g, 215 mmol), phthalic anhydride (42 g, 285 mmol), ethylene glycol (17 g, 270 mmol), propylene glycol (20 g, 270 mmol), and xylene (12 ml).
2. Purge the flask with dry nitrogen and place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, Dean-Stark trap, and reflux condenser (Figure 4.1b).
3. Place a nitrogen bubbler on the top of the reflux condenser, allowing a slow, steady stream of dry nitrogen to pass through.
4. Irradiate the reaction mixture to 140°C for 45 min. whilst stirring.
5. Remove carefully the hot flask from the microwave reactor and pour the reaction mixture into a large glass Petri dish.
6. Allow the reaction mixture to cool to room temperature.
7. Analyse the product using gel permeation chromatography (GPC) to determine  $M_n$  and  $M_w$ . ( $M_n = 2180$ ,  $M_w = 5300$ ) and determine acid number, which is usually < 50 mg KOH/g.

## 7.5.10. Unsaturated polyester resin - polyaddition

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
 Reaction vessel (250 ml round-bottomed flask)  
 Long-neck adapter (Figure 4.1)  
 Reflux condenser

**Materials**

Maleic anhydride	9.0 g, 100 mmol	harmful if swallowed, inhaled or absorbed through the skin, corrosive - causes burns, irritant
Phthalic anhydride	14 g, 100 mmol	can cause eye and skin irritation
Ethylene glycol	1.0 g, 10 mmol	harmful if swallowed, may be harmful if inhaled or in contact with the skin, skin and respiratory irritant, severe eye irritant

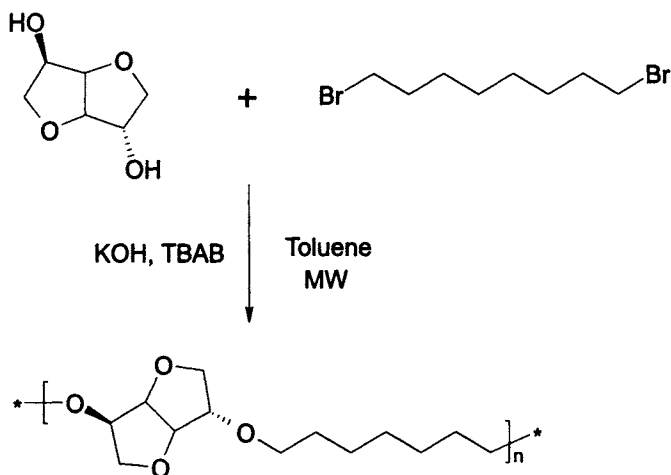
Epichlorohydrin	18 g, 200 mmol	flammable, poison, harmful if inhaled - may cause delayed lung damage, may be fatal if swallowed, reported as causing cancer in laboratory animals, causes burns, contact with eyes may cause permanent damage, long-term exposure may lead to liver or kidney damage
Lithium chloride	0.25 g, 5.9 mmol	flammable, poison, harmful if inhaled - may cause delayed lung damage, may be fatal if swallowed, reported as causing cancer in laboratory animals, causes burns, contact with eyes may cause permanent damage, long-term exposure may lead to liver or kidney damage

## Method

1. To a round-bottomed flask (250 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add maleic anhydride (9.0 g, 100 mmol), phthalic anhydride (14 g, 100 mmol), ethylene glycol (1.0 g, 10 mmol), epichlorohydrin (18 g, 200 mmol), and lithium chloride (0.25 g, 5.9 mmol).
2. Purge the flask with dry nitrogen and place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, and reflux condenser.
3. Place a nitrogen bubbler on the top of the reflux condenser, allowing a slow, steady stream of dry nitrogen to pass through.
4. Irradiate the reaction mixture to 140°C for 30 min. whilst stirring. Then increase the reactor power and heat the reaction mixture to 200°C for 5 h.
5. Remove carefully the hot flask from the microwave reactor and pour the reaction mixture into a large glass Petri dish.
6. Allow the reaction mixture to cool to room temperature.
7. Analyse the product using gel permeation chromatography (GPC) to determine  $M_n$  and  $M_w$ . ( $M_n = 920$ ,  $M_w = 3540$ ) and determine acid number, which is usually < 50 mg KOH/g.

## 7.5.11. Polyethers

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



## Equipment

Single-mode microwave reactor equipped with a pyrometer(300 W)  
 Reaction vessel (Figure 4.2b)  
 Adapter (Figure 4.2f)  
 Mechanical stirrer

## Materials

1,4:3,6-dianhydrosorbitol (isosorbide)	0.73 g, 5.0 mmol	avoid contact with skin and eyes
1,8-Dibromooctane	1.4 g g, 5.0 mmol	skin, eye and respiratory irritant, toxicology not fully investigated
Potassium hydroxide	2.0 g, 30 mmol	very hygroscopic, harmful by ingestion, inhalation and in contact with skin, if the solid or solution comes into contact with the eyes, serious eye damage may result



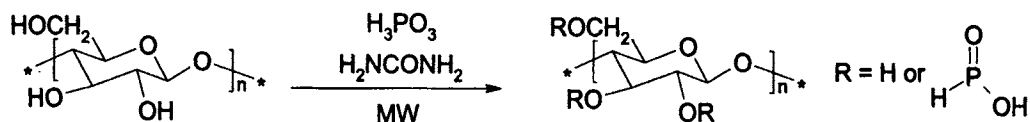
Tetrabutylammonium bromide (TBAB)	0.40 g, 1.2 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
Toluene	1.0 ml	highly flammable, toxic by inhalation, ingestion or by absorption through skin, serious irritant, experimental teratogen

**Method [121]**

1. To a clean reaction vessel add isosorbide (0.73 g, 5.0 mmol), 1,8-dibromooctane (1.4 g, 5.0 mmol), TBAB (0.40 g, 1.2 mmol), powdered potassium hydroxide (2.0 g, 30 mmol), and toluene (1 ml).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel and place it in the cavity of the microwave reactor.
4. Irradiate the mixture to 110 °C for 30 min. under mechanical stirring (Figure 4.4b).
5. Allow the reaction mixture to cool to room temperature and dilute it with chloroform (5 ml).
6. Filter the solution through a filter paper and precipitate the resultant polymer into a hexane solution (30 ml).
7. Analyse the product using gel permeation chromatography (GPC) to determine  $M_n$  and  $M_w$ . ( $M_n = 3300$ ,  $M_w = 4300$ )

**7.5.12. Phosphorylation of cellulose**

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.



**Equipment**

Single-mode microwave reactor equipped with a pyrometer(300 W)

Reaction vessel (Figure 4.2b)

Adapter (Figure 4.2f)

**Materials**

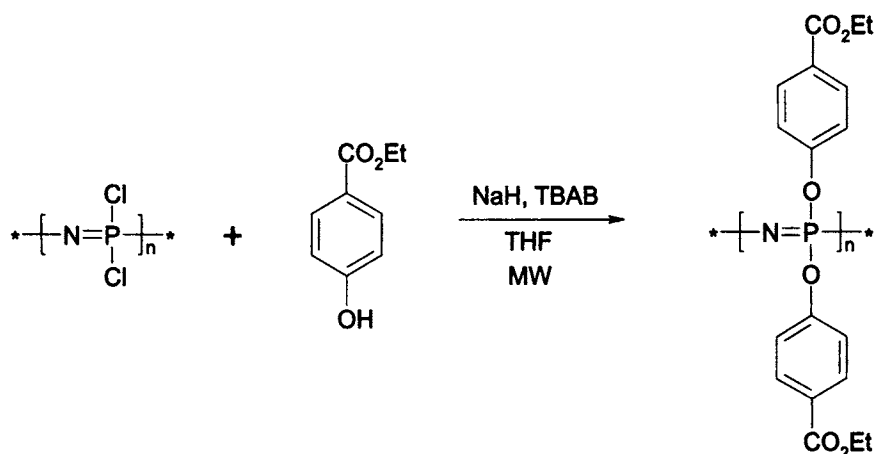
Cellulose (microcrystalline, Avicel)	0.32 g, 1.8 mmol	combustible solid, powdered material may form explosive dust-air mixtures
Urea	1.74 g, 29 mmol	irritant, prolonged exposure may cause allergic reaction in some individuals
Phosphorous acid	1.72 g, 17.6 mmol	corrosive and irritating to skin and eyes, dust is an inhalation hazard, if swallowed or inhaled, will cause burns
Water		non-hazardous
Ethanol		causes skin and eye irritation

**Method [122]**

1. To a clean and dry reaction vessel add cellulose (0.32 g, 1.8 mmol), urea (1.74 g, 29 mmol), phosphorous acid (1.72 g, 17.6 mmol).
2. Stir the mixture for 30 s with a spatula at room temperature to ensure efficient mixing.
3. Attach the adapter to the reaction vessel and place it in the cavity of the microwave reactor.
4. Rotating the reaction vessel (if possible), irradiate the mixture for 2 h to obtain a constant temperature 105°C .
5. After cooling, dissolve the reaction mixture in water and precipitate the resultant polymer into an ethanol solution.
6. Filter and dry the polymer, and repeat the purification procedure three times.

## 7.5.13. Polyphosphazene

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer (600 W)  
 Reaction vessel (250 ml round-bottomed flask)  
 Long-neck adapter (Figure 4.1)  
 Reflux condenser

**Materials**

Poly(dichlorophosphazene) (in 20 ml toluene solution)	1.0 g, 8.6 mmol	none data available
Sodium hydride (60% solution in mineral oil)	1.97 g, 49 mmol	reacts violently with water, liberating and igniting hydrogen, highly flammable, ingestion may be fatal, corrosive, skin or eye contact may cause severe burns

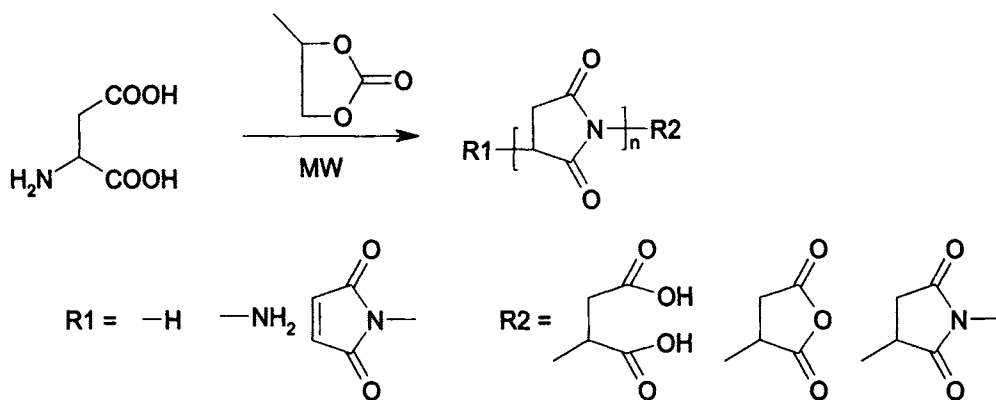
Ethyl-4-hydroxybenzoate	7.5 g, 45 mmol	may act as a skin, eye or respiratory irritant, toxicology not fully investigated
Tetrabutylammonium bromide (TBAB)	0.70 g, 2.2 mmol	harmful by inhalation or ingestion, may be harmful through skin contact, eye, skin and respiratory irritant
THF	100 ml	may generate explosive peroxides in storage if in contact with air, highly flammable, may be harmful by inhalation, ingestion or skin absorption, long-term exposure may lead to kidney or liver damage, irritant, may cause narcotic effects
Water		non-hazardous

### Method

1. To a clean and dry reaction flask (250 ml) add anhydrous THF (100 ml, ethyl-4-hydroxybenzoate (7.5 g, 45 mmol), and a magnetic stirrer bar.
2. Stir the reaction mixture with a magnetic stirrer while flushing the reaction flask with dry nitrogen, add slowly sodium hydride
3. Attach the reflux condenser, place a nitrogen bubbler on the top of the reflux condenser, allowing a slow, steady stream of dry nitrogen to pass through.
4. Reflux the reaction mixture for 30 min. whilst stirring then allow to cool to room temperature.
5. Remove the reflux condenser and add poly(dichlorophosphazene) in a 20 ml of toluene solution followed by TBAB (0.70 g, 2.2 mmol).
6. Place the flask in multi-mode microwave reactor, attach a long-neck adapter, reflux condenser, and nitrogen bubbler (Figure 4.1 and irradiate the solution up to 65°C for 2h.
7. Allow the reaction mixture to cool to room temperature and precipitate the resultant polymer from large amount of cool water(300 ml).
8. Let organic solvents evaporate, then filter and dry the polymer, and repeat the purification if necessary.

## 7.5.14. Poly(aspartic acid)

**CAUTION!** Carry out all the procedures in a well-ventilated fumehood, wear appropriate disposable gloves, labcoat, and safety glasses.

**Equipment**

Multi-mode microwave reactor equipped with a magnetic stirrer and pyrometer(600 W)  
 Reaction vessel (250 ml round-bottomed flask)  
 Long-neck adapter (Figure 4.1)  
 Reflux condenser  
 Dean-Stark trap for azeotropic distillation

**Materials**

Aspartic acid	50 g, 373 mmol	may act as an irritant can cause eye and skin irritation non-hazardous
Propylene carbonate	91 g, 892 mmol	
Water		

**Method [123]**

1. To a round-bottomed flask (250 ml) equipped with a long-necked adapter, reflux condenser, and a magnetic stirrer bar, add aspartic acid (50 g, 373 mmol), propylene carbonate (91 g, 892 mmol), and a magnetic stirrer bar.
2. Purge the flask with dry nitrogen and place the flask in the cavity of multi-mode microwave reactor, attach the long-neck adapter, Dean-Stark trap, and reflux condenser (Figure 4.1b).
3. Place a nitrogen bubbler on the top of the reflux condenser, allowing a slow, steady stream of dry nitrogen to pass through.

4. Irradiate the reaction mixture to the range of 170 to 230°C for 45 min. whilst stirring.
5. Remove the hot flask from the microwave reactor and pour carefully into a large amount of cool methanol.
6. Filter the precipitated polymer at the pump through a Buchner funnel, wash with water and dry. Yields > 70% are typical.

# Appendix

## SUBSTANCE

## HAZARDS

Acetone

highly flammable, readily forms explosive mixtures with air, harmful by inhalation, ingestion or skin absorption, irritant, liquid may cause permanent eye damage (corneal clouding), contact with skin may cause defatting, leading to irritation, long-term exposure may cause liver damage

Chloroform

causes cancer in laboratory animals, and is listed as a probable human carcinogen, inhalation and ingestion are harmful and may be fatal, may cause reproductive damage, prolonged or repeated skin contact may cause dermatitis

Cyclohexane

highly flammable, harmful if swallowed or inhaled, and through skin contact, respiratory, eye and skin irritant

Dichloromethane

harmful if swallowed or inhaled, eye and skin irritant, readily absorbed through the skin, asphyxiant, possible carcinogenic in human

Diethyl ether

extremely flammable, harmful if swallowed, inhaled or absorbed through skin, affects central nervous system

DMF	harmful by inhalation, ingestion or skin contact, may act as a carcinogen, ingestion or absorption through skin may be fatal, exposure may result in foetal death, Long-term exposure may result in kidney or liver damage, irritant
DMSO	skin, eye and respiratory system irritant
Ethanol	causes skin and eye irritation
Ethyl acetate	harmful if swallowed in quantity, vapours may cause drowsiness, irritant
Hydrochloric acid	extremely corrosive, inhalation of vapour can cause serious injury, ingestion may be fatal, liquid can cause severe damage to skin and eyes
SUBSTANCE	HAZARDS
Hexane	highly flammable, harmful by inhalation, ingestion or skin absorption, prolonged exposure may cause serious health damage
Magnesium sulfate	dust may be slightly irritating
Methanol	highly flammable, toxic by inhalation, ingestion or skin absorption, may be a reproductive hazard, ingestion may be fatal, risk of very serious, irreversible damage if swallowed, exposure may cause eye, kidney, heart and liver damage, chronic or substantial acute exposure may cause serious eye damage, including blindness, irritant, narcotic
Petroleum ether	extremely flammable, treat as harmful by inhalation or by skin contact, prolonged skin contact may cause dermatitis
Silica gel	harmful if inhaled, irritant, chronic exposure to the dust may be very harmful



Sodium hydroxide	very corrosive, causes severe burns, may cause serious permanent eye damage, very harmful by ingestion, harmful by skin contact or by inhalation of dust
Sulphuric acid	highly toxic, ingestion may be fatal, skin contact can lead to severe burns, chronic exposure may result in lung damage and possibly cancer
THF	may generate explosive peroxides in storage if in contact with air, highly flammable, may be harmful by inhalation, ingestion or skin absorption, long-term exposure may lead to kidney or liver damage, irritant, may cause narcotic effects
Toluene	highly flammable, toxic by inhalation, ingestion or by absorption through skin, serious irritant, experimental teratogen
Xylene	eye, skin and respiratory irritant, may act as a narcotic

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